

Fate and Effects of Nearshore Discharges of OCS Produced Waters

Volume II: Technical Report



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Prepared under MMS Cooperative Agreement
14-12-0001-30454

by

Louisiana Universities Marine Consortium
8124 Highway 56
Chauvin, Louisiana 70314

Published by

**U.S. Department of the Interior
Minerals Management Service
Gulf of Mexico OCS Regional Office**

**New Orleans
June 1991**

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CITATION

Suggested citation:

Rabalais, N. N., B. A. McKee, D. J. Reed and J. C. Means. 1991. Fate and Effects of Nearshore Discharges of OCS Produced Waters. Volume II. Technical Report. OCS Study/MMS 91-0005. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Regional Office, New Orleans, Louisiana, 337 pp.

COVER ILLUSTRATION

Aerial photograph of the East Timbalier Island study area with produced water treatment facilities. There are currently four active discharges and one discontinued discharge. Two discharges are generated on the Federal OCS. Black and white print of a color infrared photograph taken at 7000 feet by Wayne Grip of Aero Data Corporation. Orientation to the north.

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ABSTRACT

While the number of facilities that discharge OCS produced waters into coastal environments of Louisiana are few in number, they account for large volumes, individually and collectively. A total of 253,994 bbl·d⁻¹ of produced waters originating on the Federal OCS are piped ashore for treatment and discharge in Louisiana State waters (estimates as of March 1991). The number of OCS-generated discharge points in State waters numbered 15 at the end of our field studies in February 1990. (This number has since changed.) The newly calculated volume of 253,994 bbl·d⁻¹ based on operator estimates as of March 1991 now represents 13% of all produced waters discharged into Louisiana's waters (cf. 22% by the previous estimate in Boesch and Rabalais 1989a).

Of the 15 facilities which discharge OCS-generated produced water into coastal environments of Louisiana (as of February 1990), 10 discharges in seven areas were studied. The discharge volumes of the study areas range from 3,000 to 106,000 bbl·d⁻¹. The receiving environments for these effluents are varied, but include the shallow, nearshore continental shelf; high energy, freshwater distributaries of the Mississippi River delta; and brackish and saline coastal environments with moderately to poorly flushed waters. All study areas are within the Mississippi River Deltaic Plain. This study expanded on the initial assessment of Boesch and Rabalais (1989a) with increased temporal and spatial studies of three areas, additional study sites including an abandoned discharge, and additional analytical and field observations.

In each area, an assessment of the fate and effects of produced water discharges was made along with a detailed analysis of the effluent. The receiving environment was characterized with respect to the hydrographic regime and the sedimentary characteristics. Hydrographic profiles, interstitial salinity of surface sediments and overlying water contaminants were examined to determine the extent of the brine effluent and its chemical constituents. Likewise, surficial sediments were examined to assess the extent and composition of chemical contamination. Vertical sediment cores provided information on the long-term accumulation of chemicals. Biological impact assessments included benthic community analyses and the bioaccumulation of produced water origin contaminants by filter-feeding bivalves.

Several factors determine the fate and effects of produced waters in coastal environments and organisms. These include the volume and composition of the discharge and the hydrologic and physical characteristics of the receiving environment. Two study areas are characterized as having a high potential for dilution of contaminants: Emeline Pass and Eugene Island Block 18. On the other end of the continuum is the Pass Fourchon study area where current velocities are consistently negligible and the potential for sediment entrainment and transport is low. The remainder of the environments (Bayou Rigaud, East Timbalier Island, Romere Pass and Empire Waterway) are characterized as having a medium potential for dilution of produced water contaminants.

Produced water discharges vary greatly in the amounts of organic and inorganic compounds. Similar compounds are found in each of the effluents, but the relative proportions differ with the facility and through time. Comparisons of the produced water discharges can be made by calculations of loadings of particular contaminants. The mass loadings reflect both the volume of the discharge and the concentration of the various chemical constituents; relative differences in these loadings were helpful in understanding some of the fates of these contaminants in the various receiving environments.

A clearly identifiable density plume from the produced water effluents was present to 800 m at the Pass Fourchon study area and for a limited distance (100 m) at the East Timbalier Island area. Otherwise, no clear salinity signals were found that could be attributed to a

produced water effluent. Elevated levels of VH, sulfides and total Ra indicated dispersion of the brine effluent into the bottom waters to varying distances within the various study areas.

Substantial contamination of fine-grained sediments with petroleum hydrocarbons of produced water origin was observed at all study areas with the exception of Emeline Pass and the active discharge facility at Empire Waterway. The location of the discharge in both of these locations, as well as the high energy nature of the receiving environment at Emeline Pass, may account for lack of a contaminant signal. Elevated levels of alkylated PAH were found to the maximal extent of the study transects at both Bayou Rigaud and Pass Fourchon, 1300 and 1000 m, respectively. More limited distances were found for elevated levels of alkylated PAH at Romere Pass (450 m), East Timbalier Island (250 m), Eugene Island Block 18 (250 m) and the abandoned discharge at Empire Waterway (250 m). The presence of high concentrations of produced water derived hydrocarbons in subsurface sediments and to depths of 25 to 30 cm in a vertical sediment core in some of the study areas indicates the long-term accumulation of these contaminants and their resistance to degradation.

Severely depressed benthic macroinfaunal communities were found within 500 to 800 m of the discharge point in Pass Fourchon. Impacts to the benthic communities were observed as far as 700 m in Bayou Rigaud, 300 m at Eugene Island Block 18, 100 m at East Timbalier Island, and within 550 m of the abandoned discharge at Empire Waterway. Benthic community impacts were associated with distance from the discharges and levels of produced water chemical constituents in the sediments. The bioaccumulation studies show the clear potential for uptake and accumulation of produced water origin contaminants by oysters, both in close proximity to the discharge point and to great distances (350 m) from the discharge.

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LIST OF ABBREVIATIONS

The following abbreviations may be used throughout this report:

AEC	acid-extractable compounds
AF	accumulation factor
Al	aluminum
As	arsenic
Ba	barium
bbl	barrel
BR	Bayou Rigaud
Cd	cadmium
COTR	Contracting Officer's Technical Representative
Cr	chromium
CTD	conductivity/temperature/depth (oceanographic sensors)
Cu	copper
DBT	dibenzothiophene
DCM	dichloromethane
dpm	disintegrations per minute
EI	Eugene Island Block 18
EP	Emeline Pass
EPA	Environmental Protection Agency
EW	Empire Waterway
FFPI	Fossil Fuel Pollution Index
GC/MS	gas chromatograph/mass spectrometer
HC	hydrocarbons, usually total saturated hydrocarbons
Hg	mercury
LSU	Louisiana State University and A&M College, Baton Rouge
LUMCON	Louisiana Universities Marine Consortium
MMS	Minerals Management Service
nd	not detected
Ni	nickel
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollutant Discharge Elimination System
OCS	Outer Continental Shelf
PAH	polynuclear aromatic hydrocarbons
Pb	lead
pCi	picocurie
PF	Pass Fourchon
ppb	parts per billion
ppm	parts per million
ppt	parts per thousand
Ra	radium
RCRA	Resource Conservation and Recovery Act
RP	Romere Pass
rpm	revolutions per minute
R/T	ratio of resolved to total hydrocarbons
T	East Timbalier Island
TB	Tank Battery
Th	thorium
TOC	total organic carbon
tr	above background but below precision limit of method
TRI	Technical Resources, Inc.
UCM	unresolved complex mixture

**LIST OF ABBREVIATIONS
(Continued)**

V	vanadium
VH	volatile hydrocarbons
VOA	volatile organic analysis
Zn	zinc

CONVERSIONS

1 bbl = 42 gallons = 159 liters

dpm ÷ 2.2 = pCi

ACKNOWLEDGEMENTS

The initiative for this research program was provided by Dr. Donald F. Boesch, who was instrumental in the procurement of funds and in the development of the overall study design. The research program could not have proceeded without the cooperation of the oil and gas industry. The companies provided information about produced water discharges and facilitated access to study areas; these included Chevron U.S.A. Inc., Chevron Pipe Line Company, Exxon Pipeline Company, Conoco Inc., and Shell Offshore, Inc. Dr. Murray S. Brown served as the MMS Contracting Officer's Technical Representative (COTR) for much of the project and Dr. James J. Kendall completed the program as COTR. Ms. Gail Rainey LeBlanc was the MMS Contract Inspector.

We thank the captains, C. Black and W. Simoneaux, and crew, C. LeBoeuf, S. LeBoeuf and W. DeLaune, of the R/V *Acadiana* for assistance in sampling. Many research and laboratory assistants helped with field work and sample analyses, L. Smith, D. Smith, A. Neville, L. Hyde, A. Innes, L. Brunet and E. Gibson of LUMCON and T. Romaire and J. W. Ma of LSU. Aerial photography and prints of the study areas were provided by W. Grip of Aero Data Corporation.

R. Hughes of LUMCON helped with data management and graphics. P. Swarzenski and S. Cenac of LUMCON drafted figures. D. Eschete, S. Cenac and L. Bonvillain prepared the manuscript.

Chapter 1

INTRODUCTION

1.1 Background

During the production of crude oil, condensates or natural gas, water that is trapped within permeable sedimentary rock may also be brought to the surface. This water is called formation water, produced water or oil field brine. The water must be removed from the oil, condensate or gas as completely as possible in order to transport and use the product. This is conventionally done by pressurization and gravity separation. Water removal may also be enhanced by heat treatment or the use of demulsifiers. The separated produced water may be reinjected down a well, either for disposal or to enhance recovery of hydrocarbons, or as is the case of the vast majority of production from the northern Gulf of Mexico region, they may be discharged into the surface waters of the ocean or coastal areas.

The environmental effects of the disposal of produced waters into surface waters are the subject of increasing concern, and there is a critical need for information on the fate and effects of produced water discharges into coastal environments of the Gulf of Mexico. Produced waters generally have concentrations of dissolved salts much higher than sea water. In addition, produced waters may contain elevated levels of various inorganic (e.g., trace metals, sulfide and elemental sulfur) and organic (petroleum hydrocarbons and partially oxidized organics) substances. The discharge of produced waters into the offshore and estuarine waters of Louisiana and Texas is extensive, involving the estimated discharge of 3.4 million barrels per day from over 1500 sites (see Section 2.1). [A barrel = 42 gallons or 159 liters.] Although the discharges into the waters of the Outer Continental Shelf (OCS) are regulated by the Environmental Protection Agency (EPA) under the National Pollutant Discharge Elimination System (NPDES), the discharges into state waters, including the nearshore zone, bays and estuaries, are not subjected to similar regulatory scrutiny by federal environmental agencies. Within the State of Louisiana, the Department of Environmental Quality, Water Pollution Control Division governs all discharges to surface waters. The regulatory climate is changing rapidly because of increased concern by state agencies and as an outgrowth of recent determinations by EPA to pursue NPDES permitting in lieu of consideration of produced waters as hazardous wastes under the Resource Conservation and Recovery Act. The 1986 EPA general permit for produced water discharges in the Federal OCS will expire in 1991 and is being rewritten. Additional EPA permitting requirements are being developed for coastal waters. Recently (March 1991), a Louisiana joint legislative committee approved the plan of the Louisiana Department of Environmental Quality to phase out the majority of oil field brine discharges along the Louisiana coast in the next four years. Exceptions will be for open bay disposal, and the remaining discharges will meet new effluent limitations and habitat considerations.

Approximately 95% of the oil and 98% of the gas produced from the OCS comes from the central and western regions of the Gulf of Mexico. Much of the water produced in this process is separated and discharged from offshore production platforms. As mentioned above, EPA applies Best Practicable Treatment guidelines under the NPDES general permits for these discharges. However, of the estimated 1 million barrels per day of produced water generated on the Gulf OCS, a significant portion is piped ashore with the oil or gas streams and separated at shore-based or nearshore facilities. Approximately $254,000 \text{ bbl} \cdot \text{d}^{-1}$ of this volume is discharged into surface waters within the State of Louisiana's coastal and estuarine environments. This practice is employed for several reasons: 1) large water volumes are produced from fields not far removed from shore; 2) it is more cost effective to collect production from many wells or several fields for separation; and 3) it is more costly to construct and operate separation facilities on

offshore platforms, especially in deep water. The discharge of OCS-generated produced waters in Louisiana State waters represents 13% of all produced waters discharged in Louisiana's waters. The total of OCS-generated produced waters is 30% of all produced waters discharged into all environments of the Gulf of Mexico (see Section 2.1).

In order to provide an initial evaluation of the environmental effects of the discharge of produced waters generated on the Federally-controlled OCS but discharged into shallow coastal waters under State jurisdiction, a study was undertaken as a component of a larger Minerals Management Service (MMS)-funded study on "Impacts of Outer Continental Shelf (OCS) Related Activities on Sensitive Coastal Habitats" for which Coastal Environments, Inc. served as prime contractor (Wicker et al. 1989). The Louisiana Universities Marine Consortium (LUMCON) performed the produced water component of that study and presented the results in a report (Boesch and Rabalais 1989a). This study found that the facilities discharging OCS produced water into coastal environments of the Gulf of Mexico are limited to Louisiana and are few in number but account for large volumes, individually and collectively. Three areas with large volume discharges were investigated by field sampling. Substantial contamination of fine-grained bottom sediments with petroleum hydrocarbons was observed within several hundred meters to over one kilometer of the discharges. Concentrations of polynuclear aromatic hydrocarbons (PAH) exceeded apparent background levels by over an order of magnitude. The extent of sediment contamination was greater than observed in previous field studies (Boesch and Rabalais 1989a) because of the large volume of discharges at the three areas and the lower rate of physical dispersion in the bayous and channels into which the discharges took place. Biological effects were evident in terms of reduced density of macrobenthic organisms in contaminated sediments and the accumulation of petroleum hydrocarbons in the tissues of filter-feeding bivalves.

Because of the findings of the general study by Boesch and Rabalais (1989a) and the obviously increasing need for information useful in the prudent regulation of OCS-related discharges, the Minerals Management Service provided funds for a follow-up study to provide information on more areas than investigated in the first study and to provide greater resolution of the fates and effects of produced waters discharged from these facilities. This report presents the results of the study.

In the interim of the Boesch and Rabalais (1989a) study and the conclusion of this MMS-funded research, two programs to assess the fate and effects of produced waters generated within the State of Louisiana's jurisdiction and discharged into estuarine and wetland environments were completed (Boesch and Rabalais 1989b, St. Pé 1990). The first study, funded by The Louisiana Division of the Mid-Continent Oil and Gas Association, focused on produced waters discharged into tidal wetlands: a fresh marsh environment within the Bayou Sale oil field in the Atchafalaya Basin; a brackish marsh environment within the Lafitte field in the Barataria Basin; and a brackish-saline transitional marsh within the Golden Meadow field in the Terrebonne-Timbalier Basin. At each study site a major produced water discharge (3,000 to 4,000 bbl·d⁻¹) was selected as the focal point of remote sensing analyses and field studies. The St. Pé (1990) study was designed to examine the fate and effects of produced water discharges in low-energy, brackish marsh environments. Four sites were located within the Lirette, Delta Farms, Bully Camp and Lake Washington oil fields. The discharge volume varied from 462 bbl·d⁻¹ to 13,458 bbl·d⁻¹.

1.2 Goals of Study

The previous MMS funded study (Boesch and Rabalais 1989a) documented the general nature and extent of environmental contamination and biological effects at three major areas of OCS-generated produced water discharges: Bayou Rigaud, Pass Fourchon and East Timbalier Island. In general, this study found that sediment contamination and associated effects on the

benthos extended beyond the region in which acutely lethal concentrations of contaminants would be expected to be found in waters receiving the dispersing plume. It also found that the limit of documentable contamination of the sediments was often set by an abrupt change in the depositional regime and sediment grain size. Together, these observations suggest that the dispersal of contaminants associated with fine-grained sediments is the most likely mechanism for environmental contamination and effects beyond those in the immediate effluent mixing zone and possibly beyond those easily observable in the nearfield.

With this background in mind, the following goals of this study were identified:

- 1) Characterize the chemical composition of OCS produced waters discharged at coastal facilities in order to understand the variability.
- 2) Better define the spatial and possible temporal scale of impacts at the three areas previously studied (Boesch and Rabalais 1989a).
- 3) Characterize the effects of produced water discharges from other OCS separation facilities located in different environments in the State's coastal environments (e.g., Mississippi River delta region, nearshore Gulf of Mexico).
- 4) Characterize the dispersion of contaminants in produced waters by field measurements of tracers of dissolved substances (e.g., salinity and radium).
- 5) Characterize the bioaccumulation of contaminants to marine organisms in the field.

With these goals in mind and based on the results of previous studies, the following questions were addressed:

- 1) How do the concentrations of hydrocarbons and other organic compounds, trace metals, and radionuclides vary among discharges? How do the concentrations of these contaminants vary as a function of time and as a function of separation and treatment technology?
- 2) At what distance do the dissolved concentrations of potentially toxic contaminants reach levels which are not acutely toxic to marine organisms in receiving waters which have "flow-through" tidal exchange, as compared to "dead-end" water bodies?
- 3) At what distance do the concentrations of medium molecular weight hydrocarbons adsorbed onto particles and particle-reactive trace metals reach background levels in receiving waters which have "flow-through" tidal exchange, as compared to "dead-end" water bodies into which discharges are made?
- 4) To what degree are contaminants accumulated with depth into the sediments and how does this vary with the sediment accumulation rate and the hydrological conditions of the receiving waters?
- 5) What are the fates of radionuclides in the produced water discharges? Do they provide a better indication of the transport of contaminants away from the discharge than the hydrocarbons and trace metals?
- 6) At what concentration of polynuclear aromatic hydrocarbons (PAH) in surface sediments is there a reduction of the density and diversity of benthos? When these conditions are exceeded, are there seasonal fluctuations in benthic communities, or do changes in PAH concentrations still influence the benthic community?

- 7) At what time periods and spatial scales are petroleum hydrocarbons, trace metals and radionuclides accumulated to an equilibrium level by filter feeding bivalves exposed to dispersing produced water discharges? Are tissue concentrations of hydrocarbons elevated above ambient concentrations beyond the region of identifiable sediment contamination?

1.3 Organization of Study

The lead organization for the study was the Louisiana Universities Marine Consortium with a subcontract to the Institute for Environmental Studies, Louisiana State University and A&M College (LSU), Baton Rouge, Louisiana. An additional subcontract was let from LSU to California State College, Long Beach.

The Program Manager for the study was Dr. Nancy N. Rabalais (LUMCON). Overall direction for the study, development of study design, implementation and completion of field collections, oversight for completion of analyses, synthesis of results, and completion of reports, data products, and deliverables were her responsibilities.

Four Principal Investigators were responsible for the collection of data, laboratory analyses, data management, and interpretation of results for their respective fields of expertise. All investigators participated in the synthesis and interpretation of results.

1) Biological Assessments: Dr. Nancy N. Rabalais (LUMCON). Sampling and analysis for benthic macroinfauna, sampling and analysis of standard water quality parameters, hydrogen sulfide, and interstitial salinity of surficial sediments.

2) Chemical Assessments: Dr. Jay C. Means (LSU). Oversight of collection and analysis of hydrocarbon and trace metal analyses, bioaccumulation studies of selected contaminants, quality assurance/quality control of hydrocarbon contaminant analyses, synthesis and interpretation of hydrocarbon contaminant data. The trace metal analyses were performed under the direction of Dr. Ken Jenkins, Molecular Ecology Institute, California State University, Long Beach. The Principal Investigator for Chemical Assessments (Jay C. Means) was responsible for the interpretation and synthesis of trace metal results.

3) Radiochemistry: Dr. Brent A. McKee (LUMCON). Collection and analysis of water and sediment samples for radionuclides, and determination of sedimentation rates.

4) Currents and Sedimentary Characteristics: Dr. Denise J. Reed (LUMCON). Current measurements, determinations of bed shear stress, interpretation of results in relationship to dispersion of pollutants and sediments from the study area, sediment total organic carbon analyses, and sediment grain size analyses.

The Chief Scientist for Synthesis and Interpretation was Dr. Donald F. Boesch (formerly LUMCON, currently Center for Environmental and Estuarine Studies, University of Maryland System). He was responsible for the conceptual development, scientific development, data interpretation, and overall synthesis of the multi-faceted aspects of the research program. A synthesis team of all principal investigators, as well as Dr. Boesch and Dr. Thomas W. Duke (TRI) participated in the completion of the final synthesis product.

Data management, assistance with preparation of appropriate data products, and deliverables for NEDRES was the responsibility of the LUMCON Computer Technician, Mr. Robert Hughes. Photomissions were flown by Mr. Wayne Grip of Aero Data Corporation. Additional aerial photographs were provided from the archives of Aero Data.

Chapter 2

STUDY DESIGN

2.1 Available Sites

There are 15 facilities which have been identified as discharging OCS-generated produced water into coastal environments (volumes reported as of 02/90 at the end of our field studies, Table 2.1). All of these are located in Louisiana (Figure 2.1). Except for a few small volume discharges in Cameron Parish and another in Freshwater Bayou in southwestern Louisiana, most are found in the Mississippi River deltaic region from Atchafalaya Bay to the Mississippi River delta proper (Figure 2.1). Since identifying the discharges available for study, we have conferred with the operating company for verification or used existing permit applications from the Louisiana Department of Environmental Quality to determine the volume of produced waters discharged. The operators of the facilities that were designated for field studies provided estimates for volumes discharged at the time of field collections and/or for a 25-month period from February 1988 - February 1990. These volumes are reported in Table 2.1. In addition, revised estimates as of March 1991 were provided by the operators for some of the discharges. Since completion of our field studies in February 1990, one of the OCS-generated discharges has been redirected to the OCS (T-1 in Table 2.1) and another has been completely directed to another facility (PF-1 OCS in Table 2.1). In addition to the OCS discharges, we also identified produced water discharges in the vicinity that were not generated on the Federally-controlled OCS (Table 2.2).

Verification of discharge volumes for OCS-generated discharges, where available, provided new data for calculations of total discharges in the northern Gulf of Mexico (Table 2.3). The total volume discharged is very similar between this study and Boesch and Rabalais (1989a), but the revised estimate (03/91) for OCS-generated produced waters discharged into Louisiana coastal waters is less than in Boesch and Rabalais (1989a) by approximately 181,000 $\text{bbl}\cdot\text{d}^{-1}$. The discrepancy in OCS discharges into State waters is not a general reduction in volume, but a clarification from the operators as to the point of origin of the produced waters treated and discharged from a single facility. For example, the total volume discharged daily from the Eugene Island Block 18 Platform M is 21,000 bbl , but of that amount only 100 $\text{bbl}\cdot\text{d}^{-1}$ are generated on the OCS (Table 2.1). Two other facilities (Sabine Terminal and East Bay Central Facility, Table 2.1) also do not discharge entirely OCS-generated produced waters. The relative proportion of all OCS-generated produced waters discharged in Louisiana's State waters has decreased accordingly from the estimates in Boesch and Rabalais (1989a). Our most current estimates (as of March 1991) indicate that 253,994 $\text{bbl}\cdot\text{d}^{-1}$ of produced waters originating on the Federal OCS are piped ashore for treatment and discharge in Louisiana State waters (Table 2.3). This represents 25% of the produced waters generated on the Federal OCS. These OCS-generated discharges represent 13% of all produced waters discharged into the State's waters (based on volumes reported as of 03/91 in Tables 2.1 - 2.3).

2.2 Site Selection

From the list of facilities (Table 2.1) which process OCS produced waters, a selection of 10 facilities in seven study areas was made for field studies by joint consultation of the principal investigators and MMS representatives. A set of primary and secondary study areas, along with an abandoned site, was chosen for study. Two of the areas studied previously (Boesch and Rabalais 1989a) were selected as primary study areas for increased spatial and temporal studies. The third area sampled previously was included as a secondary study area, but with increased spatial coverage. Four additional locations were included as secondary study areas.

Given the difficulties anticipated in sampling the Mississippi River within Southwest Pass and the expected dilution of contaminant signal in that system, the Shell East Bay Central Facility (Table 2.1) was dropped from consideration as a study area. Those in the southwestern part of the state were excluded because of their small volume discharges.

2.2.1 Primary Study Areas

Two locations were selected for seasonal and intense spatial sampling. These areas were sampled in the Boesch and Rabalais (1989a) study on two occasions in 1987-1988 and displayed considerable sediment contamination.

Bayou Rigaud is the location of large discharges of OCS produced water at the Conoco Grand Isle Shore Base and the Exxon Grand Isle Station.

Pass Fourchon at the time of the field studies received two OCS produced water discharges and a discharge generated in State waters. Changes in handling of product streams has occurred at all three facilities, but a large combined volume is still discharged at the location (see Section 5.1.2).

2.2.2 Secondary Study Areas

Additional areas were selected because they represented the range of coastal environments receiving OCS produced waters and because of the size of the discharges. The secondary study areas were sampled on one or two occasions.

East Timbalier Island is the location of several produced water discharges of significant volume. At the time of the field studies, two were discharging OCS-generated produced waters (T-1, T-2 in Table 2.1). [One of these (T-1) has since been rerouted to the OCS (as of March 1991).] A third discharge, which had been generated on the OCS, was discontinued in 1988. In the general area for field studies, two additional discharges handle State-generated produced waters (Table 2.2). (See Section 9.1.1 for detail of the study area.)

Eugene Island Block 18 is the location of a platform in the territorial sea just offshore of the remnant oyster reefs which demark the lower end of Atchafalaya Bay. The platform, situated in 2 to 3 m of water on the shallow continental shelf, is undoubtedly influenced by alternate deposition of sediments from the Atchafalaya River and wave scour of deposited sediments. Platform M, which discharges OCS-generated produced waters, also handles product streams from several wells in State waters (Table 2.1).

Emeline Pass and Romere Pass are two study areas located in the Mississippi River delta proper. Both areas are either in or near a main tributary of the river. A single facility in Emeline Pass handles OCS produced waters (Table 2.1). The facilities located on Romere Pass handle, treat and discharge separate effluents of OCS-generated produced waters and one of produced waters generated in the State jurisdiction.

Empire Waterway is the location of a facility which currently discharges OCS-generated produced waters, as well as an abandoned discharge site (see below).

2.2.3 Abandoned Site

The Exxon Pelican Island Terminal was located on a dredged canal with access to Empire Waterway. The facility is no longer in operation, and, at the time of the field studies, was being dismantled. When discharging, the volume reported was an estimated 12,000 to 15,000 bbl·d⁻¹ as recently as 1986. When we were developing this study, it was the only

abandoned OCS discharge we were able to identify by comparison with reported discharges by Gianessi and Arnold (1982) based on 1976 surveys. Since the initiation of this study, we learned that the discharge at Chevron South Timbalier Block Tank Battery 35 has ceased. In addition, since the end of our field studies, an OCS discharge at Tank Battery 21, 27, 28 in the East Timbalier Island study area has been rerouted offshore (see Section 9.1.1), and the product stream for PF-1 OCS has been routed to the PF-2 OCS facility (see section 5.1.1).

2.3 General Study Design

The sampling strategy outlined below was designed to expand what had been documented for the three areas examined in the previous study (Boesch and Rabalais 1989a), to extend these studies to additional areas for a better understanding of other OCS separation facilities, to provide additional information on the composition of produced water and to examine the bioaccumulation of selected organic and inorganic contaminants.

2.3.1 Station Location and Sampling Frequency

The study areas varied significantly from each other in the number of discharges, in the amount of produced waters discharged, in the characteristics of the receiving environments, in the sedimentary and tidal regimes and in the associated habitat modifications. Because of this, potential sampling arrangements depended, to a great extent, on the relationship of the produced water discharge points to adjacent water bodies. Generalized sample designs were proposed, but the precise details of the station positioning awaited examination of aerial photographs and, sometimes, the actual visit to the field for collections to accommodate the particular physiographic and environmental characteristics of the sites.

Table 2.4 outlines the number of stations and dates of samples for the study areas. The station locations and sample dates were designed to provide maximum information about a variety of areas and detailed information about a few. Optimal distances from the discharge point for station locations were 0 m, 50 m, 100 m, 250 m, 500 m and 1000 m. The final locations for some of the stations were determined by the geography and physiography of the study area. Aerial photographs of each potential area were examined prior to site selection and field collections. Existing 27.5' quad maps were inadequate for the rapidly changing Louisiana coastal zone. Photomissions for high resolution, color infrared large format photography at 7,500-ft altitude provided 16" x 20" prints and standard slides. A low altitude flight at 1,000 ft provided additional color photography for selection of stations. Transparent overlays were placed on the aerial photographs and stations marked prior to field collections. The photographs were taken to the field, and changes in the station locations were made after comparing the locale and the photographs.

Primary Study Areas

At Bayou Rigaud and Pass Fourchon, we conducted seasonal sampling, with the seasons being dictated by biological phenomena. We sampled in the late winter (February) during which time we expected to find high recruitment of juvenile macroinfauna to benthic communities. The second sample period was in the late spring when we expected the peak recruitment period to have ended and the populations to be in decline, either from reduced food availability, increased competition, or increased predation pressure. The third seasonal sample was in the fall (October-November) when predation pressure was expected to decline. We followed up with an additional late winter sample in the second year to examine year-to-year variability. Bayou Rigaud was the most intensely studied area with respect to spatial variability. The Pass Fourchon site was studied similarly for spatial variation but the number of stations was reduced.

Secondary Study Areas

Two areas were sampled during expected high and low flow of the Mississippi and Atchafalaya Rivers. These were the Grand Bay Receiving Station in Emeline Pass, a major tributary of the Mississippi River, and the Eugene Island Block 18 Platform M just offshore of Atchafalaya Bay in the influence of the Atchafalaya River.

The remaining secondary study areas were sampled once. At the East Timbalier Island study area an increased number of stations was added to improve the spatial coverage from the previous study (Boesch and Rabalais 1989a). The number of stations in Romere Pass and at the West Delta Terminal near Empire Waterway were more similar to the other study areas.

Abandoned Site

The Exxon Pelican Island Terminal was selected for examination as an abandoned site. There were five stations at this site to be sampled once; one of the five stations could not be sampled because of an obstruction in the access canal. The Pelican Island Terminal is near Empire Waterway, where a currently active OCS-generated produced water discharge is located.

2.3.2 Surveys of Contaminants and Biota

Within each of the study areas, a series of stations was designed for a general assessment of the fate and effects of the produced water discharge(s) in the receiving environment. An outline of the type of samples and data collected at each type of station is given in Table 2.5. Samples and data collected at the "primary stations" were also collected at the "secondary" stations. The design was supplemented at the secondary stations with samples of near-bottom water and vertical sediment cores. Any exceptions to this general sample design are noted in the study area chapters. Detailed sample methodology is given in Chapter 3.

The general characteristics of the water column in the study area were determined. Hydrographic profiles for standard water quality parameters were taken at each station. These included water depth, temperature, conductivity, salinity, pH and dissolved oxygen. Hydrogen sulfide (H_2S) was tested for in selected near-bottom waters of the receiving environment where any clear signal of elevated salinities and/or low dissolved oxygen levels were detected. In order to better characterize the receiving environments, water currents were measured at a station near a discharge point during the environmental assessment.

At each study area, produced waters and the near-bottom waters of the receiving water column were examined for contaminants. Produced waters generally have concentrations of dissolved salts much higher than sea water. In addition, they may contain elevated levels of inorganics (trace metals and sulfide) and organic (e.g., petroleum hydrocarbons) substances (Neff et al. 1989). Produced waters may also contain concentrations of radionuclides several times higher than typical coastal and marine waters (Reid 1983). Produced waters from the discharge points were sampled for salinity, hydrocarbons, trace metals, radionuclides and sulfides. The water column overlying the bottom near the discharge point and at selected stations along a gradient away from the discharge point were sampled for hydrocarbons and radionuclides.

Surficial (10 cm) sediments were sampled at primary and secondary stations along a gradient away from the discharge for interstitial salinity, and hydrocarbon, trace metal and radionuclide (Pb-210) contaminants. At secondary stations, sediment cores were also collected for vertical distribution of hydrocarbons, trace metals and radionuclides. Sulfides were not analyzed in sediments, since all sediments contain concentrations of sulfides under anaerobic conditions. Radium was not analyzed in sediments since it was expected to be soluble in the

water column. Observations of high Ra-226 activities in sediments examined from stations near produced water discharges in brackish environments (St. Pé 1990) may be attributed to methodological techniques in which the sediments were dried with interstitial waters intact prior to analysis for the radionuclide.

In order to properly characterize the receiving environments, to place the level of contaminants in context and to explain possible macroinfaunal distributions, general analyses of sedimentary characteristics were made. These included sediment total organic carbon (TOC), sediment grain size, and sedimentation rate measurements. Sediment grain size samples were analyzed from surface sediments at each station. Where vertical cores were taken, sediment grain size samples were taken for each 5-cm section down the core. Sediment TOC samples were taken for surface sediments, as well as a few blind replicates for quality control.

Bed sediments may serve as a temporary reservoir of particles available for resuspension into the water column and/or as a permanent burial site for particles (and associated contaminants). Selected radionuclides (Pb-210 and Th-234) can be used as tools to determine rates of sedimentary processes in bed sediments (Koide et al. 1973, Nittrouer et al. 1979). Individual radionuclides differ in their characteristic time scale of interest. This time scale is approximately five times the half life of the radionuclide. Therefore, Pb-210 (22 year half-life) is useful in examining sedimentation rates over a 100-year time scale. Similarly, the flux of particle-reactive radionuclides can be examined over a range of time scales. This is accomplished by measuring the concentration profile of each radionuclide with depth in core, and calculating the time-averaged flux needed to maintain the observed concentration inventories in the seabed. By this method, the depth to which particles (and particle-reactive radionuclides) are buried at a site can be determined for 100-year time scales using Pb-210.

Bottom sediments were sampled for benthic macroinfauna along the same gradients as outlined above for sedimentary characteristics.

2.3.3 Bioaccumulation of Selected Contaminants

One of the objectives of this study was to examine the potential impacts of organic and inorganic contaminants associated with the discharges of produced waters into coastal environments, including any potential for extension of those impacts to man through the food chain. Many of the contaminants found in produced water discharges are toxic to aquatic organisms and to man, and many of the organic compounds are known or suspected mutagens or carcinogens. An aspect of this study, therefore, was to address the bioaccumulation potential of these contaminants. The approach used was to deploy an indigenous population of filter-feeding bivalves (the American oyster, *Crassostrea virginica*) at known distances from the discharge points for known periods of time. Similar designs have been used in several large-scale biomonitoring studies in estuarine environments (Farrington et al. 1983, Neff et al. 1976, NOAA 1987). Two deployments were made at the Pass Fourchon and Bayou Rigaud study sites in April and May for 14 and 27 days, respectively.

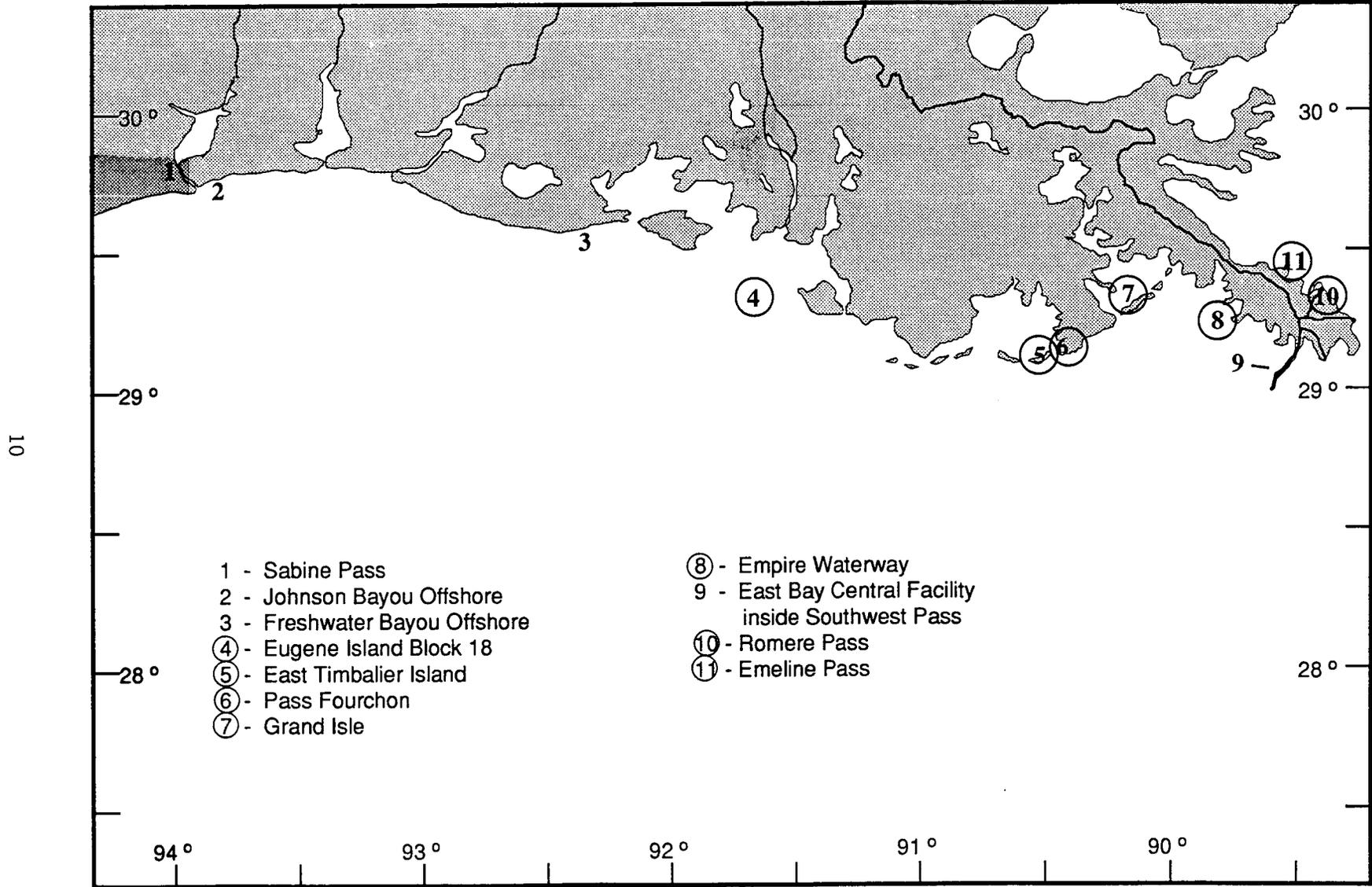


Figure 2.1. General location of OCS-generated produced water discharges in Louisiana State waters with circled numbers indicating areas studied.

Table 2.1. Facilities in the Louisiana coastal zone which discharge produced waters emanating from the Federally-controlled outer continental shelf (as of 02/90). Number in left margin keyed to general location in map in Figure 2.1. Location names in (parentheses) refer to discharge labels used in subsequent chapters. [A barrel = 42 gallons = 159 liters.] (Modified from Boesch and Rabalais 1989a.)

	Facility	Location	Company	Discharge (bbl·d ⁻¹)
1	Sabine Terminal	Sabine Pass	Chevron U.S.A. Inc.	288** (OCS = 24)
2	Johnson Bayou Tank Battery	Cameron Parish	Chevron U.S.A. Inc.	500
2	West Cameron Block 45	Johnson Bayou Cameron Parish	Phillips	2,100**
3	Texas Gas Sales	Freshwater Bayou	Union	10
4	Eugene Island Block 18	Platform M	Shell Offshore, Inc.	21,000* (OCS = 100)
5	Tank Battery 21,27,28	East Timbalier Island (T-1)	Chevron U.S.A. Inc.	13,258* 0**
5	Tank Battery 36,37	East Timbalier Island (T-2)	Chevron U.S.A. Inc.	5,005* 8,500**
6	Fourchon Terminal	Pass Fourchon (PF-2 OCS)	Chevron Pipe Line Co.	4,768* 32,500**
6	Bay Marchand Barge	Pass Fourchon (PF-1 OCS)	Chevron U.S.A. Inc.	9,645* 0**
7	Grand Isle Station	Bayou Rigaud	Exxon Pipeline Co.	40,000*
7	Grand Isle Shore Base	Bayou Rigaud	Conoco	105,760*
8	West Delta Block 30 Terminal	Empire Waterway	Chevron Pipe Line Co.	10,959* 15,000**
9	East Bay Central Facility	Southwest Pass/ Mississippi River	Shell Offshore, Inc.	185,000** (OCS = 38,000)
10	Main Pass Block 41 Terminal	Romere Pass/Main Pass (RP-1 OCS)	Chevron Pipe Line Co. Chevron U.S.A. Inc.	3,021* 5,000**
11	Grand Bay Receiving Station	Emeline Pass	Chevron U.S.A. Inc.	3,693* 6,500**

* Volume discharged is an average of monthly discharge rates for period 02/88 - 02/90 (data from operator).

** Volume discharged as of 03/91 (data provided by operator).

OCS = volume discharged of total volume that is generated on the OCS.

Table 2.2. Facilities in the Louisiana coastal zone with discharges of produced waters emanating from State waters but which were located near or in the vicinity of those discharging produced waters generated on the Federal OCS (as listed in Table 2.1). Number in left margin keyed to general location in map in Figure 2.1. Discharge names in (parentheses) refer to labels used in subsequent chapters.

Facility	Location	Company	Discharge (bbl·d ⁻¹)
5 Tank Battery 2	East Timbalier Island	Chevron U.S.A. Inc. ***	4,866
5 Tank Battery 3	East Timbalier Island	Chevron U.S.A. Inc. ***	2,429*
6 Fourchon Terminal	Pass Fourchon (PF-2 State)	Chevron Pipe Line Co.	33,756* 32,500**
10 Romere Pass State	Romere Pass/Main Pass (RP-2 State)	Chevron U.S.A. Inc.	17,137* 20,000**

* Volume discharged is an average of monthly discharge rates for period 02/88 - 02/90 (data provided by operator).

** Volume discharged as of 03/91 (data provided by operator).

*** Sold to another oil and gas operator since initiation of this study.

Table 2.3. Comparisons of estimates of produced water discharges (bbl·d⁻¹) from this study and that of Boesch and Rabalais (1989a).

		<u>OCS-Generated</u>		<u>State-Generated</u>		Total
		OCS Disposal	Louisiana State Coastal Disposal	Louisiana State Coastal Disposal	Texas State Coastal Disposal	
Boesch and Rabalais (1989a)	Volume	745,228	434,772	1,524,962	735,854	3,440,816
	Percentage	22%	13%	44%	21%	
This Study (as of 02/90)	Volume	750,900	236,843	1,698,448	735,854*	3,422,045
	Percentage	22%	7%	50%	21%	
This Study (as of 03/91)	Volume	764,158	253,994	1,700,055	735,854*	3,454,061
	Percentage	22%	8%	49%	21%	

* No new estimates.

Table 2.4. Number of primary, secondary and current meter stations in each study area and the number of produced water discharges collected for the various sample periods.

	Sample Period			
	2/89	4-5/89	10-11/89	2/90
<u>Primary Study Areas</u>				
Pass Fourchon				
Primary Stations	6	11	6	6
Secondary Stations	6	6	6	6
Discharge	3	3	3	3
Current Meter	1	1	1	1
Bayou Rigaud				
Primary Stations	11	21	11	11
Secondary Stations	6	6	6	6
Discharge	3	2	2	2
Current Meter	1	1	1	1
<u>Secondary Study Areas</u>				
Emeline Pass				
Primary Stations		11	11	
Secondary Stations		6	6	
Discharge		1	1	
Current Meter		1	1	
Eugene Island Block 18				
Primary Stations		9	11	
Secondary Stations		5	5	
Discharge		1	1	
Current Meter		1	1	
East Timbalier Island				
Primary Stations		15		
Secondary Stations		6		
Discharge		2		
Current Meter		1		
Romere Pass				
Primary Stations			8	
Secondary Stations			4	
Discharge			2	
Current Meter			1	
West Delta 30 Terminal near Empire Waterway				
Primary Stations			6	
Secondary Stations			3	
Discharge			1	
Current Meter			1	
<u>Abandoned Site</u>				
Pelican Island Terminal near Empire Waterway				
Primary Stations			4	
Secondary Stations			3	
Discharge			0	
Current Meter			0	

Table 2.5. Generalized scheme for types of samples and data collected at primary and secondary stations, from discharge points, and at current meter stations in all study areas. Symbols are used in study area maps in the appropriate chapters.

Station Designation	Sample Type, Data
Primary Station ●	CTD Profile Surface Sediments Grain Size Distribution Total Organic Carbon Interstitial Salinity Semivolatile Hydrocarbons Trace Metals Radionuclides Benthic Biota
Secondary Station ◎	As above, plus: Near-Bottom Water Volatile Organic Analysis Semivolatile Hydrocarbons Radionuclides Hydrogen Sulfide Vertical Sediment Core Grain Size Distribution Semivolatile Hydrocarbons Trace Metals Radionuclides, Sedimentation Rates
Discharge ▲	Salinity Sulfide Volatile Organic Analysis Semivolatile Hydrocarbons Trace Metals Radionuclides
Current Meter ■	26-hr Current Direction and Velocity

Chapter 3

METHODS

3.1 Field Logistics

3.1.1 Vessel and Boat Support

Depending on the study site, a combination of LUMCON's coastal vessel the R/V *Acadiana* and small boat support was used. The selection of vessel depended on the receiving environment for the produced water discharge, whether into dredged canal, open shallow bays, or a main distributary of the Mississippi River delta. The *Acadiana* was used as a staging vessel for all the field trips. Small boats were used for access to stations inaccessible to the deeper draft vessel. A 22-ft Aquasport was the primary boat used for the current meter measurements. During adverse weather conditions, these data were taken from on board the *Acadiana*.

3.1.2 Sampling Equipment

Three box corers were used from the *Acadiana*. One was an Ekman-type closure, 0.1-m² box corer with an average penetration of 20 cm and a minimum penetration of 10 cm in sandy, well-sorted sediments. A second 0.1-m² Ekman-type box corer averaged a penetration of 50 cm in soft sediments and a minimum of 30 cm in sandy sediments. A third corer was a spade corer, 0.06-m², with an average penetration of 50 cm and a minimum of 20 cm in sandy, well-sorted sediments. When shallow water or narrow waterways precluded the navigation of the *Acadiana*, sediment samples were taken with a small (0.025-m²) hand-operated Ekman grab.

A Hydrolab Surveyor II water quality monitoring system was used for gathering hydrographic information. Near-bottom water samples were collected with a horizontally-mounted, messenger-tripped 30-l Niskin bottle deployed from the *Acadiana*. Verification of near-bottom water salinity from the Niskin sample with a refractometer compared to that of the Surveyor II CTD unit readings assured that water samples were taken as near the bottom as possible. A horizontally mounted 2-l Alpha water sampler was used from the small boats.

3.2 Hydrography and Currents

3.2.1 Hydrographic Profiles

At all stations, water column measurements were made at 1-m (sometimes 0.5-m) intervals with a Hydrolab Surveyor II CTD unit for water temperature, salinity, conductivity, pH and dissolved oxygen. Water samples for verification of conductivity measurements were taken for salinity determinations on an AGE "Minisal" Model 2100 salinometer. Pre- and post-cruise calibration of the Hydrolab over the last three years of operation in various LUMCON research programs has verified it as a reliable instrument. The Hydrolab sonde unit was replaced mid-way through the project. The new unit performed equally well.

3.2.2 Sulfides

The determination of sulfides was done spectrophotometrically according to the methods outlined in Parsons et al. (1984). Since hydrogen sulfide is volatile and any sulfide is rapidly oxidized by dissolved oxygen in water or upon exposure to air, precautions were taken to ensure proper sample collection. Samples were drawn into tightly stoppered reagent bottles using a long Pasteur pipet affixed to the water bottle with rubber tubing. Water for sulfides, when collected, was taken from the Niskin bottle first. Samples were fixed immediately and stored in

a dark, cool place until analysis, which took place 20 min later. The combination of spectrophotometer light path length and reagents provided for an accurate range and precision of $3 \pm 0.22 \mu\text{g-at S}\cdot\text{l}^{-1}$ to $40 \pm 3 \mu\text{g-at S}\cdot\text{l}^{-1}$. Limitations of this methodology to the stated range indicated trace amounts (tr) of sulfide at values of 1 to $3 \mu\text{g-at S}\cdot\text{l}^{-1}$; sulfide was not detected (nd) at readings below $1 \mu\text{g-at S}\cdot\text{l}^{-1}$ which would be similar to background levels.

3.2.3 Current Velocity Profiles

Current velocity profiles at a station were characterized by monitoring for a 25-hr period during the main field surveys. Current speed and direction was measured with a Braystoke BFM 108 current meter fitted with a compass and depth sensor. Data were recorded by hand from the surface readout unit. Readings were taken every 30 min at a minimum of four discrete depths through the water column. The bottom reading was 25 cm above the bed and the uppermost, 25 cm below the water surface. The monitoring was usually conducted from a small boat at a fixed location. During adverse conditions, measurements were taken from the R/V *Acadiana* which changed in station according to progress with other sampling. The current profiles have been used to calculate shear velocities (U_*) using Karman-Prandtl methodology (Leeder 1982).

3.3 Sedimentary Characteristics

3.3.1 Interstitial Salinity

Surface sediments from the upper 1 cm were collected with a small syringe, placed in a small centrifuge vial, refrigerated and returned to the laboratory for analysis. In the laboratory, the samples were centrifuged. The supernatant (usually a 10- μl sample) was analyzed on a digital chloridometer (Haak Buchler). A standard correction for chloride ions in sea water was used for conversion to salinity values.

3.3.2 Grain Size Distributions

Surface grain size samples were taken using 60-cc piston core subsamples. Samples were bagged and kept on ice before air drying in the laboratory. Vertical grain size samples were taken from 7.5-cm diameter cores. They were sectioned into 1-cm slices with the first cm of every 5 cm being retained for analysis, e.g. 0-1 cm, 5-6 cm, 10-11 cm, etc. for the length of the core. Sliced subsamples were air dried and ground before analysis.

Grain size distributions were determined using a Coulter Multisizer with 256 channelizer capability. This instrument allows rapid processing of samples and accurate particle sizing down to $0.3 \mu\text{m}$. Three aperture tube sizes were used in the analysis: $280 \mu\text{m}$, $140 \mu\text{m}$ and $50 \mu\text{m}$. Samples were sieved through 20- μm Nitex before analysis with the 50- μm aperture tube. Coulter Accucomp software was used to overlay distributions from each tube, and sand, silt and clay fractions were identified using the final combined distribution. Coarser samples were also sieved to isolate larger sand particles unsuitable for Coulter Multisizer analysis. Where appropriate these sand measurements were combined with the Coulter Multisizer data, assuming a constant particle density for the sand fraction, to produce a total grain size distribution. Grain size is described according to the sand, silt and clay fractions. In characterizing sediment grain size, silt and clay fractions are frequently combined and described as mud.

3.3.3 Total Organic Carbon (TOC)

Surface samples for TOC analyses were taken using 60-cc piston core subsamples. Samples were bagged and kept on ice before air drying in the laboratory. Samples were ground and carbonate material was removed using hydrochloric acid. Subsamples for analysis were weighed on a Cahn micro-balance. The analysis was conducted using a Control Equipment

Elemental Analyzer, Model 240XA with a multisampler injector. Duplicate samples for the maximum and minimum TOC readings for each study area were performed for quality control.

3.4 Produced Water Salinity and Sulfides

Salinity of water samples of the produced water discharge was determined by a potentiometric chloride titration on a digital chloridometer (Haak Buchler). A standard correction for chloride ions in sea water was used for conversion to salinity values. Comparisons were made with a temperature-compensated refractometer, but the chloride-determined values were recorded in the data tables (Appendices A and C).

Sulfides were determined immediately upon collection of the sample according to the spectrophotometric methods outlined for near-bottom water samples in Section 3.2.2.

3.5 Hydrocarbon Analytical Methods

Sediment samples were collected in 7.5-cm core tubes from the various box corers. Those samples taken from a small boat were collected with 7.5-cm core tubes mounted on a pole with a "core catching" device at its end. The cores were stored on ice until return to the laboratory where they were stored frozen until analysis.

3.5.1 Sediment Extractions

The sediment extraction method was a modification of that described by MacLeod et al. (1985). After thorough mixing, 10-15 g of wet sediment was weighed to 0.01 g into an amber bottle fitted with a Teflon-lined cap. The bottles were centrifuged at 2,000 rpm for 10 min, and excess moisture decanted. Seventy-five milliliters (75 ml) of dichloromethane (DCM), 50 g sodium sulfate, and 4 µg each of a mixture of deuterated standards (surrogate spike, Table 3.1) were added to the bottle. Contents of the jar were mixed using a spatula, then tightly capped and shaken, making sure contents were loose and did not stick to the sides of the jar. Twelve samples, including a duplicate and PAH-spiked sample, and a reagent blank were prepared at one time. The jars were placed on a modified rock tumbler (Lortone, Inc., Seattle, WA) and tumbled overnight. The DCM from each jar was decanted into a 240-ml amber jar and refrigerated. Another 75 ml aliquot of DCM was added, and the jars were tumbled for 6 hr, followed by decanting. A third aliquot of DCM was added, and tumbled overnight. The decanted DCM was filtered through funnels packed with sodium sulfate into 300-ml round bottom flasks and rotary evaporated to approximately 2 ml. The concentrated extract was transferred to a 4-ml vial and further concentrated with solvent exchange to hexane to a final volume of 500 µl. Fine granular copper was added to reduce sulphur interferences. Extracts from the tumbling procedure were not subjected to further cleanup or fractionation. Analysis of the "whole" extract allowed for simultaneous estimation of aromatic and aliphatic hydrocarbon concentrations. Polar compounds, such as phenols and acids, were not analyzed because these compounds are: 1) not efficiently extracted with this method, 2) less persistent than other components of produced water in sediments and 3) produced in sediments by microbial processes, therefore making it difficult to distinguish contributions from biological and petrogenic sources. Reagent blanks, duplicates and PAH-spiked samples were analyzed to monitor laboratory technique and extraction efficiency. Sample extracts showing less than 50% recovery of d10-phenanthrene (surrogate spike) after duplicate GC/MS analyses were re-extracted. A laboratory reference sediment, consisting of a mixture of sediments collected at various locations in South Louisiana and spiked with South Louisiana Crude Reference Oil (U.S. EPA-API) and six parent PAH compounds, was repetitively extracted and analyzed to measure reproducibility of the extraction and analysis methods.

A 3-5 g subsample of wet sediment was taken for dry weight determination. The wet sediment was dried in an oven at 90°C until a constant dry weight was obtained from which the

percent moisture value was calculated. Sample weights for hydrocarbon determinations were corrected for moisture content. Analyte concentrations are reported on a dry weight basis.

3.5.2 Volatile Organic Analysis of Waters

Water samples for volatile organic analysis (VOA) were stored at 5°C until analysis. All samples were analyzed within 5 days of receipt by a purge and trap/gas chromatography (GC) technique similar to EPA Method 624. The instrumentation used was a Tekmar LS-2 purge and trap interfaced to a Hewlett Packard 5890 GC equipped with a 30 meter J&W 624 megabore capillary column and a flame ionization detector (FID). Quantitative results were based on an external standard method using authentic standards and a 3-point standard curve. Quantitative results were based on an external standard method using authentic standards and a 3-point standard curve. Compounds quantified using this method are referred to as volatile hydrocarbons (VH). Naphthalene is quantified as both a volatile and semivolatile because it displays appreciable volatility at room temperature making it difficult to quantify accurately by either method. Naphthalene is a part of both the totals graphed for volatiles and semivolatiles. When naphthalene and its alkylated analogs are discussed, naphthalene values are from semivolatile calculations.

3.5.3 Water Extractions for Semivolatile Hydrocarbons

Samples were extracted by a liquid-liquid extraction method similar to EPA Method 625 except only an acid/neutral extraction was performed. Surrogate standards of d5-phenol, d5-1,4-dichlorobenzene, d8-naphthalene, d10-acenaphthene, d10-phenanthrene, d12-chrysene, and d12-perylene were added to each sample prior to extraction. One liter aliquotes were adjusted to pH <2 with sulfuric acid (1:1) and extracted three times with 60 ml of dichloromethane (DCM). Extracts were filtered through funnels packed with sodium sulfate into 500-ml round bottom flasks. Sample extracts were first reduced in volume to 2 ml using a rotary evaporator and then brought to a final volume of 1 ml (effluent samples) or 200 µl (overlying waters) under a stream of purified nitrogen. Extraction blanks were analyzed to verify adequate glassware cleanliness and solvent purity. Duplicate and spiked samples were extracted to verify analytical recoveries and ensure reproducibility.

A 100-µl aliquot of the produced water extracts was separated into two fractions by silica gel chromatography. The F1/F2 fraction, containing the aliphatic hydrocarbons and polynuclear aromatic hydrocarbons (PAH), was eluted with DCM/hexane (1:1) and the F3 fraction, containing polar compounds, was eluted with methanol. The fractions were reduced under a stream of purified nitrogen to a final volume of 200 µl. Overlying water samples were not fractionated.

3.5.4 Oyster Extractions

Oysters were collected from the field and placed on ice until return to the laboratory. All live oysters in each sample were opened and separated in the following manner: approximately 100 g were set aside for extraction, two oysters were frozen and saved for trace metal analysis, one was weighed, dried and reweighed for dry weight data, and the remaining were frozen in a glass jar. Oysters were not depurated prior to analyses, but the pseudofeces were removed by rinsing with organic-free water. Frozen samples were later thawed, homogenized and 10 g sent for radionuclide analysis. The remaining homogenized samples were frozen. The oysters that were set aside for extraction were weighed, frozen in liquid nitrogen and minced in a blender with sodium sulfate and a small amount of dry ice. These powdered samples were maintained frozen in glass jars until tissue extraction.

The tissue extraction method described in MacLeod et al. (1985) was followed with some modification. A 75-g subsample of the sodium sulfate/oyster tissue mixture was extracted with

450 ml of dichloromethane (DCM) (150 ml of DCM added three times in each extraction). After each addition of DCM the sample was homogenized with a Tissue Tearor at approximately 25,000 rpm for four minutes after which the DCM was decanted through a funnel filled with sodium sulfate into a 500-ml florence flask. After three extractions the decanted DCM was reduced in volume by rotary evaporation to approximately 2 ml. The extract was transferred to a 4-ml vial and further concentrated with solvent exchange to hexane to a volume of 2 ml under nitrogen. From each sample, 200 μ l was transferred to a pre-weighed aluminum pan and dried for 24 hr at 90°C and then reweighed to obtain percent lipid analysis. One half of the remaining extract was separated from the polar lipids on 300 mm x 13 mm columns packed with 9 g of PR grade Florisil, eluted with 100 ml of 40% DCM and 60% hexane and concentrated under nitrogen to 200 μ l final volume. Extracts were analyzed by GC/MS for the PAH listed in Table 3.1, with the exception of PAH with molecular weights greater than 252.

3.5.5 Semivolatiles Instrumental Analysis

Sediment extracts, oyster extracts, near-bottom water extracts and the F1/F2 and F3 fractions of the produced water discharge samples were analyzed using a Hewlett Packard 5890 GC equipped with a J&W 30 meter DB-5 capillary column, 0.25 mm inside diameter and 0.25 micron film thickness, directly interfaced to a Hewlett Packard 5970B Mass Spectrometer. Quantifications were based on an internal standard technique compared to authentic standards where available and corrected for recoveries of the surrogate standards. To ensure reproducible instrument performance, the MS was tuned daily using the autotune program. Column performance was verified by the use of a Grob standard (Grob et al. 1978), internal standards and standards of the analytes of interest.

Quantitative determination of the semivolatiles target compounds listed in Table 3.1 utilized an extracted ion/internal standard method similar to methods described in EPA Method 625. The primary ion in Table 3.1 was used for quantitation, while the secondary ion was used to confirm identification. The target compounds were chosen because of: 1) their relative abundance in petroleum sources such as crude oil and production water; 2) their potential to rapidly partition into the sediment and accumulate due to their low water solubilities; and 3) their relative persistence in the environment. In addition to the petrogenic compounds, common pyrogenic compounds (i.e. fluoranthene, pyrene and higher molecular weight PAH) were qualitatively and quantitatively identified to aid in differentiating the contaminant source. The surrogate deuterated standards were used to correct for recovery. The homologous series components, C1- and C2-naphthalenes, C1-dibenzothiophenes, and C1- and C2-phenanthrenes, were quantified with a standard mix of these alkylated homologs. The C3-, C4-, and C5-naphthalenes, C1- through C3-fluorenes, C2- and C3-dibenzothiophenes and C3-phenanthrenes were estimated by extracted ions using the response factor of representative compounds. The minimum detection limit (MDL) was calculated for each sample, based upon the minimum detectable amount of phenanthrene, as determined from a standard curve, corrected for recovery of d10-phenanthrene and the dry weight of the sample.

Sums of groups of analytes are reported in Appendices C, D and H. "Total Parent PAH" refers to the sum of the 17 parent, or non-alkylated PAH, that were targeted by the analysis method. This sum is sometimes referred to as pyrogenic PAH; components having their source from the combustion of fossil fuels, although some parent compounds, such as naphthalene and phenanthrene are also components of crude oil. The sum of alkylated PAH includes all levels of alkylation determined using authentic standards or estimation, and includes several classes not included in previous studies: C4- and C5-naphthalenes, and C1- through C3-fluorenes. These additional classes of analytes were determined to be important constituents of the petroleum hydrocarbons found in sediments collected as part of this study, however, they are not part of the FFPI calculation described below. "Total PAH" is the sum of "Total Parent PAH" and "Total Alkylated PAH."

The "fossil fuel pollution index" (FFPI) (Boehm and Farrington 1984) indicates the relative percentage of petroleum-derived hydrocarbons in the measured total PAH. This index is based on the distribution of PAH in petroleum, which contains a relative abundance of alkylated homologs of naphthalene, phenanthrene and dibenzothiophene compared to their unalkylated parent compounds. Crude oil would have an FFPI of about one (1). The FFPI is a continuum, which decreases with a decrease in petroleum-derived hydrocarbons and/or an increase in pyrogenic hydrocarbons. The index is a useful tool in studies monitoring the impact of petroleum-derived PAH. The FFPI is determined by the following formula modified from Boehm and Farrington (1984):

$$\text{FFPI} = [\Sigma \text{naphthalenes (C}_0\text{-C}_3) + \Sigma \text{dibenzothiophenes (C}_0\text{-C}_3) + \\ 1/2 \Sigma \text{phenanthrenes (C}_0\text{-C}_1) + \Sigma \text{phenanthrenes (C}_2\text{-C}_3)] / \Sigma \text{PAH}$$

C_n = number of alkyl carbons substituted

ΣPAH = sum parent PAH and alkylated naphthalenes, dibenzothiophenes, and phenanthrenes.

Saturated hydrocarbons were determined by an extracted ion/internal standard method using mass 57. An estimation of the total saturated hydrocarbons (aliphatics), total resolved saturated hydrocarbons, and total unresolved saturated hydrocarbons was determined using a response factor based upon a standard containing nC-15 to nC-30 alkanes, pristane, phytane, and squalane and d10-phenanthrene as a surrogate standard. Total resolved hydrocarbons were determined by a valley-to-valley integration technique, total saturated hydrocarbons by integrating the entire chromatogram, including the unresolved complex mixture (UCM), as a single peak. The total unresolved saturated hydrocarbons were determined by subtracting the resolved saturated hydrocarbons from the total.

The ratio of Resolved to Total Hydrocarbons (R/T) was calculated and presented in the appendix tables to show the degree of weathering of saturated petroleum hydrocarbons. Higher values (near 1.0) indicate a predominance of normal alkanes which means little weathering has occurred, while values approaching zero indicate a high degree of weathering, and display an increase in the proportion of the UCM as the simpler, straight-chain hydrocarbons are degraded.

3.6 Trace Metal Sample Analysis

A 3-g subsample of sediment was transferred to an acid washed plastic bottle and then frozen. The frozen sediment samples, oyster samples and produced water samples were shipped to the Molecular Ecology Institute at California State University, Long Beach. After receipt, sediment, water and tissue samples were stored at -80°C until processing. Each sediment sample was thawed to room temperature for approximately 15 min and samples individually homogenized using a Teflon spatula. A 1-g aliquot was removed and transferred to an individual polypropylene 20-ml digestion container. The samples were oven dried for 24 hr at 60°C from which water contents and dry weights were calculated. The dry sediment samples were digested using a CEM Microwave Digestion system by addition of 2.5 ml concentrated HNO₃, and digesting for 3 hr at a mean power setting of 300 watts. A 4-ml aliquot of each produced water sample was removed and transferred to a culture tube for direct metal analysis.

Oyster samples were thawed, minced using Teflon forceps, and homogenized in metal-free ground glass homogenizers (hand-held) until a uniform consistency was obtained. Two subsamples were removed, one for acid digestion and metal determinations (minimum 0.5 g wet weight) and one for dry weight determination. Dry weight subsamples were transferred to a pre-weighed crucible, oven-dried (90°C for 24 hr) weighed, and then ignited (550°C for 2 hr), and the

ash-free dry weight obtained. The subsample aliquot for metal determinations was transferred to a metal-free polypropylene digestion vessel for digestion as described above for sediments, using 0.5-g tissue in 10 ml concentrated HNO₃. Digests were diluted to 100 ml prior to removal of an aliquot for analysis.

A procedural blank and a sample of Standard Reference Material marine sediment (NRC MESS-1) or NBS oyster tissue were processed with each batch of ten samples. Resulting digestants were quantitatively transferred, brought to a final volume of 50 ml and a 4 ml aliquot analyzed for: Al (aluminum), V (vanadium), Cr (chromium), Ni (nickel), Cu (copper), Zn (zinc), As (arsenic), Cd (cadmium), Ba (barium), Hg (mercury) and Pb (lead). Sample digestants were spiked with an 100 ppb Yttrium as an internal standard. Samples were analyzed using a VG PlasmaQuad Inductively Coupled Plasma Mass Spectrometer (ICP/MS). In addition to the standard ICP/MS configuration, the instrument was equipped with a water-cooled spray chamber and ETP dynode detector to optimize sensitivity and stability and minimize background noise. Samples were calibrated using regression statistics based on the analysis of five aqueous metal standards including 0.1, 1.0, 10.0, 100.0 and 1000.0 ppb (ng/ml) of the eleven metals.

Standard laboratory protocols for sample analysis using ICP/MS techniques include two reagent blanks and one aqueous metal sensitivity standard (100 ppb) per approximately 10 environmental samples. Additionally, three samples of SRM trace metals in fresh water are analyzed for each analytical run. All environmental samples, standard reference materials, procedural and reagent blanks were analyzed at the same time on the ICP/MS for an identical suite of metal isotopes. The data are reported as µg metal/g dry weight (ppm) for sediments and ng metal/ml water (ppb) for water samples. These values are corrected for any artifacts indicated by procedural and reagent blanks. Produced water discharges were analyzed for 11 trace metals; however, only nine of these metals have been reported. The data for Al and As were not reported, because the high salt background caused interference in the analyses.

3.7 Radiochemistry

Produced waters may contain concentrations of radionuclides several times higher than typical coastal and marine waters (Reid 1983). These radionuclides are usually introduced via produced waters as very soluble isotopes (e.g., Pb-210, Th-228, Th-234) that are sorbed onto particle surfaces and subsequently follow the pathways of the particles. In this study, concentrations of soluble (Ra-226, Ra-228, U-234, U-238) and particle-reactive radionuclides (Pb-210, Th-228, Th-234) were measured in produced waters (both dissolved and particulate phases). The uranium and thorium isotopes precede Ra-226 in the natural decay chain; therefore, their presence or absence in produced waters is a good indicator as to whether the strong radium signal observed in produced waters is due solely to original radium discharged or is also supported by parent radionuclides.

Water samples from near-bottom of the water column and the produced water effluent were divided into two aliquots: (a) for Pb-210, U-238 and Th-234 analyses; and (b) for total radium (Ra-226 + Ra-228) analyses. Sediment subcores were extruded and subsectioned at 1-cm intervals downcore for Pb-210 analyses. All radionuclide data are presented as disintegrations per minute. For comparison to values of radioactivity reported in the literature as picocuries, the conversion from disintegrations per minute (dpm) to picocurie units (pCi) is $dpm \div 2.2 = pCi$.

Radium isotopes from water samples were concentrated onto Mn-impregnated fiber and counted directly via gamma spectrometry on an intrinsic germanium detector (Michel et al. 1981). For uranium, thorium and lead analyses, water samples were acidified to pH 2. Ferric chloride and yield tracers were added and the pH raised to pH 8 to co-precipitate uranium, thorium and lead from the sample with iron hydroxide. Yield tracers for uranium, thorium and lead were added to dried core samples and the samples were leached with a combination

perchloric, nitric and hydrochloric acids. Thorium and uranium were isolated via ion exchange methods (Aller and Cochran 1976, McKee et al. 1986), and Pb-210 was plated onto silver planchets and measured via the polonium method (Nittrouer et al. 1979). Thorium was plated onto stainless steel planchets and counted by low level beta spectrometry. Pb-210 (via Po-210) and uranium were counted by alpha spectrometry. Total radium is the sum of Ra-226 and Ra-228 activities. The ratio of Ra-226/total Ra varies with produced water discharge, but in most cases the Ra-226 activity constitutes more than two-thirds of the total radium activity.

None of the Pb-210 vertical sediment profiles were acceptable for calculating sedimentation rates. To calculate sedimentation rates, some decay in Pb-210 downcore must be observed. This is done by plotting the decreasing activities of excess Pb-210 with depth in core. The slope of this decreasing profile with depth reveals the rate of sediment accumulation. In the cores examined for this project, no significant decrease in Pb-210 activity downcore was noted at any of the sites. The profiles were either very scattered with depth or indicated increasing activity levels with depth. We think that these profiles are due to a combination of: (a) disturbance of the natural primary sedimentary structure due to dredging and resuspension by boats; and (b) a decrease in Pb-210 input from produced waters over the past 50 years, perhaps due to decreased discharge or decreased Pb-210 content of discharged waters.

One way to examine the flux of Pb-210 to sediments is to calculate sediment Pb-210 inventories. Pb-210 sediment inventory is the total Pb-210 activity present in the core collected ($\text{dpm}\cdot\text{cm}^{-2}$). Under steady state conditions, the sediment inventory multiplied by the decay constant for Pb-210 ($0.031\cdot\text{yr}^{-1}$) determines the Pb-210 flux required to support the observed inventory within the core examined. In natural environments, the atmosphere is, by far, the dominant source of Pb-210 to sediments, supplying about $1\text{ dpm}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$. Because the Pb-210 activities do not decrease to a background level for the cores examined in this project, the inventories calculated from these cores give a minimum estimate of the Pb-210 flux to the area.

3.8 Benthic Biota

Sediment samples for benthic macroinfauna analysis were taken with either of the box corers or a small, hand-operated sediment grab. Samples taken with the larger box corers were then subsampled for a 0.025-m^2 surface area to a depth of 10 cm with a hand-held Ekman grab. The entire contents of the Ekman grab were used. The volume of sediment collected was noted, if the sample appeared not to have penetrated to a suitable depth. Three replicates per station were taken.

Samples were sieved in the field through a 0.5-mm screen. If time or logistics did not allow, the samples were placed in buckets to be sieved upon return to the laboratory. The organisms retained on the sieve and debris were preserved in 10% buffered formalin in ambient water stained with Rose Bengal.

Macroinfaunal samples were transferred to the sorting laboratory at LUMCON where they were logged into a laboratory record book by sample code, number of containers per sample, and date received. In the laboratory the formalin was decanted over a 0.5-mm sieve inside a fume hood. The samples were rinsed with water and decanted a second time after settling of the organisms. The samples were sorted in water from gridded dishes under a dissecting microscope. Organisms were counted and identified to the lowest possible taxon. Organisms normally considered part of the meiofauna (nematodes and harpacticoid copepods) were not included in the macroinfaunal analysis. Data were entered into dBase data files. A collection of voucher specimens from the benthic infaunal samples was retained in a Reference Collection. The debris from the sample was rechecked by another technician for any missed organisms. If organisms were found, the sample was resorted. Quality control measures included resorting all samples.

Standard benthic community parameters were determined for each station and included number of species per replicate, number of individuals per replicate, diversity (H') and evenness (J'). Diversity was calculated by the following formula:

$$H' = -\sum_{i=1}^s \left(\frac{n_i}{N} \right) \log \left(\frac{n_i}{N} \right)$$

where s = total number of species collected, n = number of individuals of each species, and N = total individuals. Evenness was calculated by the formula:

$$J' = \frac{H'}{\log_2 s}$$

Basic statistics were computed using procedures of the Statistical Analysis System (SAS 1982).

Infaunal data were analyzed using the General Linear Models procedures for analysis of variance (SAS 1982). Data were transformed when necessary to meet the assumptions of homogeneity of variance and normal distribution. $\log_e(x+1)$ and square root transformations were performed when appropriate and are noted. Duncan's multiple range test was performed to identify significantly different stations with a group. The level of significance was established at $P < 0.05$.

3.9 Data Synthesis

The results of the field assessments were consolidated into a multi-component data base for characterizing the effects of produced waters on the water column, sediments and benthic biota. The data base was developed so that information on each station/sample date was consolidated. General hydrocarbon, trace metal and radionuclide data were combined with hydrographic data, sedimentological data and benthic community data. Standard benthic community parameters, including number of species, number of individuals and measures of species diversity were entered into the data base.

The data provided the information needed to define the spatial and temporal scale of impacts. Differences in parameters (where replicated) were tested by analysis of variance and general linear model analyses. Simple correlations and multiple regression analyses were used to relate species assemblage properties to location and environmental parameters. An overall synthesis of the fates and effects of OCS produced waters discharged into coastal waters was based on the field assessments. The synthesis addressed the differences observed as related to the magnitude of the discharges, the loadings of the discharges, the characteristics of the effluent and the characteristics of the receiving environments.

Table 3.1. Primary and secondary ions of semivolatile target compounds.

	Primary ion (m/z)	Secondary ion (m/z)
Acid-Extractable Compounds (AEC)		
d5-Phenol (surrogate spike)	99	-----
Phenol	94	66
C1-Phenols (Cresols)	108	107
C2-Phenols	122	107
Benzoic Acid	105	122
C1-Benzoic Acids	91	136
C2-Benzoic Acids	105	150
Aliphatic Fatty Acids	60	73
Polynuclear Aromatic Hydrocarbons (PAH)		
d8-Naphthalene (surrogate spike)	136	-----
Naphthalene	128	129
C1-Naphthalenes	142	141
C2-Naphthalenes	156	141
C3-Naphthalenes	170	155
C4-Naphthalenes	184	-----
C5-Naphthalenes	198	-----
Acenaphthylene	152	153
d10-Acenaphthene (surrogate spike)	164	-----
Acenaphthene	153	152
Fluorene	166	165
C1-Fluorenes	180	-----
C2-Fluorenes	194	-----
C3-Fluorenes	208	-----
Dibenzothiophene	184	185
C1-Dibenzothiophenes	198	197
C2-Dibenzothiophenes	212	211
C3-Dibenzothiophenes	226	225
d10-Phenanthrene (surrogate spike)	188	-----
Phenanthrene	178	179
C1-Phenanthrenes	192	191
C2-Phenanthrenes	206	191
C3-Phenanthrenes	220	205
Anthracene	178	179
Fluoranthene	202	101
Pyrene	202	101
Benz(a)anthracene	228	226
d12-Chrysene (surrogate spike)	240	-----
Chrysene	228	226
Benzo(b)fluoranthene	252	253
Benzo(k)fluoranthene	252	253
Benzo(a)pyrene	252	253
d12-Perylene (surrogate spike)	264	-----
Indeno(1,2,3-cd)pyrene	276	278
Dibenz(a,h)anthracene	278	276
Benzo(g,h,i)perylene	276	278

Chapter 4

CHARACTERIZATION OF PRODUCED WATERS

4.1 Background

Produced waters are one of a variety of wastes generated from oil and gas production wells (Neff et al. 1987). The volume of water produced may be quite large and often increases as the petroleum product decreases. In older fields, such as coastal Louisiana and Texas, the water content may be as high as 95% of the product stream (Neff et al. 1989).

Produced waters are usually more concentrated in salinity than normal sea water (35 ppt) ranging from 3 to 300 ppt (Rittenhouse et al. 1969). Produced waters may contain elevated levels of several metals and elemental sulfur (Neff et al. 1987). Metals found at concentrations higher than in sea water are barium, beryllium, cadmium, copper, iron, lead, nickel, silver and zinc (Neff et al. 1987). Radionuclides also occur at elevated levels in produced water discharges, primarily as Ra-226 and Ra-228 (Reid 1983). The levels of radium usually parallel the salinity of the produced water (Kraemer and Reid 1984, see Section 4.9.4) but not always (Neff et al. 1989). The total radium activity of the four samples analyzed by Neff et al. (1989) were not clearly correlated with salinity but suggested a relationship with the TOC concentration of the effluent. Free sulfide may also be elevated in produced waters and varies with the formation.

Produced waters contain high concentrations of organic compounds, primarily petroleum hydrocarbons but also partially oxidized organics. In addition, various chemicals, such as demulsifiers, clarifiers and biocides, may be added during the treatment. The petroleum hydrocarbon fraction has been most thoroughly analyzed, but additional compounds have also been examined (reviewed in Neff et al. 1987, 1989). Detailed analyses of produced waters have been presented in several studies (Armstrong et al. 1979, Sauer 1981, Neff et al. 1989, Boesch and Rabalais 1989a, b). The results of this study complement these previous studies, provide comparisons, and detail more thoroughly the semivolatile aromatic components.

The treatment of produced waters varies among facilities but may include heat treatment, gravity separation, aeration and settling ponds, and chemical additives. The purpose of the various treatments is to remove the particulate or dispersed oil in order to reduce the overall oil and grease content of the discharge. The types of treatment facilities for the produced waters studied in this program span the range of those available. Information that has been obtained from the operator of each produced water treatment facility is provided in the general description of each study area.

4.2 Pass Fourchon

The Pass Fourchon study area consisted of three discharges sampled four times: PF-1 OCS, PF-2 OCS and PF-2 State. Data presented are for averages of the four samples, unless stated otherwise.

4.2.1 Salinity and Sulfides

The average salinity of the discharges at Pass Fourchon over four sample periods was 162 ppt for PF-1 OCS, 54 ppt for PF-2 OCS and 153 ppt for PF-2 State (Table C.1). Sulfides were trace or not detected in the PF-1 OCS and PF-2 State discharges. The PF-2 OCS discharge had a high sulfide content on the two occasions it was measured (113.0 and 134 $\mu\text{g-at S}\cdot\text{l}^{-1}$) (Table C.1), which contributed to the black color of the discharge.

4.2.2 Organic Composition

The volatile fraction of all discharges at Pass Fourchon contained mainly benzene and toluene with these compounds comprising an average of 89% of the identified volatiles in PF-1 OCS, 80% in PF-2 OCS and 87% in PF-2 State (Figure 4.1 and Table C.2). These discharges probably contained other volatile compounds at low levels such as short chain normal alkanes, cyclic alkanes, other C3-benzenes, C4-benzenes and ketones. This is based on data from Sauer (1981) and mass spectral analysis of Conoco's discharge by our laboratory. The volatile compounds identified and reported here comprised 70-85% of the total estimated volatiles in these discharges, using the response factor for ethylbenzene to quantitate unidentified compounds. PF-1 OCS contained the highest total identified volatiles, followed by PF-2 State and PF-2 OCS. The relative amounts of individual components were similar for these discharges even though the total amounts varied widely between discharges. Over the four sample periods, PF-1 OCS displayed the most consistent concentration levels. The other discharges varied in concentration, which may be due in some part to sampling technique, but the large changes seen in PF-2 OCS and PF-2 State in May 1989 suggested some alteration in treatment techniques and/or efficiency of separation.

The acid-extractable fraction was the largest component of the organics measured in these discharges. Although being a small fraction of crude oil, these compounds have the highest water solubility which favors their incorporation in produced water at higher levels than the less soluble PAH fraction. This fraction contained aliphatic and aromatic acids, phenol and alkyl-substituted phenols (Figure 4.2 and Table C.2), with the organic acids making up an average of 95% of the total AEC for all Pass Fourchon discharges. The highest concentration of AEC was found in the PF-1 OCS discharge with PF-2 OCS and PF-2 State containing 60% and 85% less, respectively. All discharges contained high amounts of aliphatic fatty acids, followed by benzoic acid and alkyl-substituted benzoic acids. The phenols comprised only 3-6% of the total AEC for all three discharges. The aliphatic fatty acids displayed the highest variation in concentration during the four sample periods for all three discharges. Phenol and substituted phenol concentrations were highly variable for both the PF-1 OCS and PF-2 OCS discharges.

The saturated hydrocarbons were the organic compounds next highest in concentration after the AEC. This fraction is composed of normal straight-chain hydrocarbons (alkanes), isoprenoid hydrocarbons, branched-chain hydrocarbons and naphthenes (cycloalkanes). Saturated hydrocarbons are classified as resolved and unresolved components. The unresolved class represents petroleum oil components that cannot be fully separated by gas chromatographic methods. The resolved hydrocarbons were usually less than 50% of the total saturated hydrocarbons for all three discharges (Figure 4.3 and Table C.2). The highest concentration of saturated hydrocarbons was detected in the PF-1 OCS discharge. An increase in concentration over time was noted in the PF-2 State discharge, while there were consistent levels of saturated hydrocarbons in the discharges of PF-1 OCS and PF-2 OCS for three out of the four sample periods.

The polynuclear aromatic hydrocarbons (PAH) class was the smallest organic component of the produced water discharges. Naphthalene and its alkylated analogs were the largest PAH components in all three discharges (Figure 4.4 and Table C.3). Naphthalenes comprised 84% of the PAH for PF-1 OCS, 74% for PF-2 OCS and 67% for PF-2 State, while phenanthrenes were 7% (PF-1 OCS) to 16% (PF-2 State) of the total PAH. PF-1 OCS contained the highest concentration of naphthalenes, while PF-2 State had the most phenanthrenes and fluorenes. Based on the average PAH concentrations of the three Pass Fourchon discharges over the four sample periods and the average daily discharge rate of produced water by the facilities, the total daily amount of PAH discharged was 3.5 kg and derived from the individual daily discharges of: PF-1 OCS = 1.0 kg, PF-2 OCS = 0.1 kg, and PF-2 State = 2.4 kg (see Section 4.9).

4.2.3 Trace Metals

The trace metals found in highest concentrations in Pass Fourchon discharge samples were Ba, V, Ni and Cu (Figure 4.5 and Table C.8). Lower levels of Cr, Zn and Cd were found in all discharge samples. Pb was detected in low concentrations in the samples from PF-1 OCS and PF-2 State. Hg was detected in only two discharge samples: PF-2 OCS for February 1990 and PF-2 State for October 1989. Ba was the metal in highest concentration from the PF-2 OCS and PF-2 State discharge samples, while V was highest in PF-1 OCS. The trace metal concentrations in the PF-1 OCS discharge samples were consistent during the four sample periods, with the exception of a higher Zn value during February 1989. Ba showed concentration variations in the samples from PF-2 OCS and PF-2 State. The last two samples of PF-2 State contained Ba at concentrations greater than twice the previous sample dates.

4.2.4 Radionuclides

Pb-210: Produced waters from Pass Fourchon contained Pb-210 radioactivities ranging from 1.13 to 25.4 dpm·l⁻¹ (Figure 4.6 and Table C.9). Pb-210 is produced by the decay of Ra-226 via four short-lived intermediate daughter products. Pb-210 has a 22 year half-life and is quickly sorbed onto particle surfaces once it is produced. The Pb-210 activity for natural waters is about 0.1 dpm·l⁻¹ (range: 0.01 to 0.15). Therefore, the Pb-210 activity in Pass Fourchon produced waters was approximately 11 to 250 times higher than the surrounding natural waters. During the four periods sampled, the PF-2 State discharge had the highest Pb-210 concentrations (range: 2.71 to 25.4 dpm·l⁻¹) and the PF-2 OCS discharge had the lowest concentrations (range: 1.13 to 8.79 dpm·l⁻¹). The PF-1 discharge contained intermediate Pb-210 concentrations (7.4 to 18.1 dpm·l⁻¹). At all three discharge sites, the highest Pb-210 activities were measured during the first sampling period (February 1989). Pb-210 activities in all three discharges decreased by 3-5 fold during the following year.

Radium: Produced waters from Pass Fourchon contained total radium (Ra-226 + Ra-228) radioactivities ranging from 371 to 2312 dpm·l⁻¹ (Figure 4.7 and Table C.9). The total radium activity for natural waters is about 2 dpm·l⁻¹ (range: 0.05 to 5). Therefore, the total radium activity in Pass Fourchon produced waters was approximately 186 to 1156 times higher than the surrounding natural waters. During the four periods sampled, the PF-2 State discharge had the highest total radium concentrations (range: 1230 to 1890 dpm·l⁻¹) and the PF-2 OCS discharge had the lowest concentrations (range: 371 to 650 dpm·l⁻¹). The PF-1 discharge contained intermediate total radium concentrations (943 to 2312 dpm·l⁻¹). In all three discharges the highest total radium activities were measured during February 1989. Total radium activities in all three discharges decreased by almost a factor of two during the following year.

4.3 Bayou Rigaud

Two discharges in the Bayou Rigaud study area, Exxon and Conoco, were sampled four times. The Conoco discharge sample for February 1990 was discarded and retaken in March 1990 to correct our inappropriate selection of sample point. The Exxon discharge sample in February 1989 consisted of "Pre" and "Post" samples. The "Pre" sample was taken after leaving the primary separation tank, but before entering an open maze pond. The "Post" sample was taken from the pond as it emptied into a drainage ditch leading to Bayou Rigaud. The "Pre" sample was only taken once. Subsequent Exxon samples were collected at the "Post" location and are referred to as "Exxon." The discussion that follows concentrates primarily on the average of the Exxon Post samples to that of the average of the four Conoco samples.

Residence time of the Exxon discharge in the open pond reduced, on the average, the total VH, AEC and PAH by a factor of about 2, while reduction in saturated hydrocarbons was about 4 times. Total naphthalenes comprised 85% of the total for the Exxon Pre sample, while

the average for the four Post samples was 95%, indicating the additional treatment in the pond caused a greater reduction in other PAH over naphthalenes. Subsequent comparisons are restricted to the average of the four Post samples.

4.3.1 Salinity and Sulfides

The average salinity of the Exxon discharge over four sample periods was 100 ppt and 68 ppt for the Conoco discharge (Table C.1). The Exxon discharge had trace or non-detectable concentrations of sulfide on the two occasions tested. The Conoco discharge had elevated sulfide ($8.7 \mu\text{g-at S}\cdot\text{l}^{-1}$) on one occasion but only trace levels otherwise (Table C.1).

4.3.2 Organic Composition

The total of benzene plus toluene were 93% and 75% of the total volatiles identified for the Exxon and Conoco discharges, respectively (Figure 4.8 and Table C.4). The volatile compounds identified were 93% for Exxon, and 88% for Conoco of the total estimated volatiles. The Conoco discharge contained almost twice the amount of volatiles as Exxon. Volatile hydrocarbons concentrations for both Exxon and Conoco were very consistent over the four sample periods.

The acid-extractable compounds were 91% for Exxon and 85% for Conoco of the total organic load measured. The organic acids comprised an average of 94% of all the AEC identified in these discharges (Figure 4.9 and Table C.4). Conoco contained higher quantities of AEC of the two discharges and also displayed a steady increase in these compounds during the four sample periods. The Exxon discharge water contained very low levels of AEC in the February 1989 sample, but concentrations sharply increased during subsequent samples to about half of the Exxon "Pre" February 1989 level. Changes in some aspect of the treatment process could be responsible for this increase, but none were reported by the operator.

Saturated hydrocarbons contributed only 1% to the Exxon discharge organic load, while it comprised approximately 8% of Conoco. Resolved hydrocarbons were found to be 40% and 45% of the total for Exxon and Conoco, respectively (Figure 4.10 and Table C.4). The concentration of saturated hydrocarbons increased in the both discharges over the four sample periods.

Naphthalene and its alkyl-substituted analogs comprised 94%, Exxon, and 85%, Conoco, of the total PAH identified. However, the discharges differed in the distribution of naphthalenes, with Exxon having naphthalene and C1-naphthalenes at greater levels than the higher molecular weight naphthalenes (Figure 4.11 and Table C.5). The distribution of naphthalenes in the Conoco discharge water was more typical of produced water discharges, where C3-naphthalenes are highest in concentration. This suggests that the treatment techniques used at the Exxon facility, besides reducing the total PAH concentration to 20% of Conoco's discharge, also changes the distribution of the naphthalenes. Both discharges exhibited an increase in total PAH concentration during the year of sampling. Based on the average PAH concentration and discharge rate, there could be 9.8 kg of PAH being discharged daily into Bayou Rigaud by Conoco and 0.7 kg PAH by Exxon (see Section 4.9).

4.3.3 Trace Metals

There were no substantial differences between the "Pre" and "Post" samples of the Exxon discharge in metal content with the exception of Cd which was seven times higher in the "Pre" sample. Only the trace metals in the Exxon "Post" samples are compared with the Conoco discharge.

Ba, V and Ni were the metals found in highest concentration in both the Exxon and Conoco discharge samples (Figure 4.12 and Table C.8). Cu, Zn, Cr and Cd were detected at much lower concentrations, with Pb detected in some but not all samples and Hg not detected. The Conoco discharge water contained twice as much Ba as the Exxon discharge water. Most other metals were detected in similar concentrations in both discharges. There was no variation in metal concentrations for either discharge during the four sample periods.

4.3.4 Radionuclides

Pb-210: Produced waters from Bayou Rigaud contained Pb-210 radioactivities ranging from 0.21 to 21.1 dpm·l⁻¹ (Figure 4.13 and Table C.9). These radioactivities are about 2 to 210 times higher than natural waters. During February 1989, a "Pre" and "Post" sample of the Exxon discharge was taken. The "Pre" sample had a Pb-210 activity (27.54 dpm·l⁻¹) approximately four times higher than the "Post" sample (6.88 dpm·l⁻¹). This decrease could be due, in part, to the partial removal of particulate materials in the produced waters. Pb-210 is very rapidly adsorbed onto particle surfaces and is generally associated with the particulate fraction of a water sample. During February 1989, the Conoco discharge contained the highest Pb-210 activity (21.1 dpm·l⁻¹) compared to the Exxon "Post" discharge (6.88 dpm·l⁻¹). Subsequent samples collected from the Conoco discharge site had much lower Pb-210 activities (range: 0.20 to 0.76 dpm·l⁻¹). Pb-210 activities at the Exxon discharge site were variable over the three subsequent sampling periods (range: 0.78 to 5.37 dpm·l⁻¹).

Radium: Produced waters from Bayou Rigaud contained total radium radioactivities ranging from 304 to 1012 dpm·l⁻¹ (Figure 4.14 and Table C.9). These radioactivities are approximately 152 to 506 times higher than natural waters. During February 1989, a "Pre" and "Post" sample of the Exxon discharge had approximately the same total radium activity (Figure 4.14). During February 1989, the Exxon discharge contained the highest total radium activity (1012 dpm·l⁻¹) compared to the Conoco discharge (416 dpm·l⁻¹). Subsequent samples collected from the two discharges had lower total radium activities (range: 304 to 897 dpm·l⁻¹).

4.4 Emeline Pass

The discharge at Emeline Pass (EP) was sampled in April 1989. During the October 1989 field trip, the facility was not pumping, so a discharge sample was taken several weeks later in November 1989.

4.4.1 Salinity and Sulfides

The Emeline Pass discharge averaged 72 ppt salinity (Table C.1). For the single discharge sample analyzed, the sulfide levels were elevated (11.1 µg-at S·l⁻¹) (Table C.1).

4.4.2 Organic Composition

The volatile hydrocarbons in the EP discharge were dominated by benzene and toluene which comprised an average of 70% of the total volatiles identified (Figure 4.15 and Table C.6). The volatiles identified accounted for 55% of the total estimated volatiles for this discharge. The November 1989 sample contained almost three times the amount of volatiles found in April 1989. The acid-extractable fraction was dominated by the aliphatic and aromatic acids which made up an average of 96% for this fraction. There was no difference in the concentration of AEC between the two sample periods. The saturated hydrocarbons displayed a three-fold change in concentration from the April 1989 to November 1989 sampling. There were also differences in the percentage of resolved hydrocarbons 37% for April 1989 versus 23% for November 1989. The PAH fraction was dominated by naphthalenes with C3-naphthalenes being highest in concentration for both sample periods (Figure 4.15 and Table C.7). The naphthalenes

contributed 67% for April 1989 and 79% for November 1989 to the total PAH concentration. As with the volatile and saturated hydrocarbons, the November 1989 water sample had much higher PAH levels than water from April 1989. These differences could be the result of treatment and/or crude oil source variations. The average daily input of PAH into the environment from the Emeline Pass facility was estimated to be 1.4 kg (see Section 4.9).

4.4.3 Trace Metals

The produced water sample from Emeline Pass had Ba, V and Ni in highest concentration (Figure 4.16 and Table C.8). Lower levels of Cu, Zn, Cr and Cd were detected in this discharge. Pb was only detected in the November 1989 sample, while Hg was not detected. The concentration of Ba in the November 1989 sample was about half that found in April 1989. All other metals were at similar concentrations during both sample periods.

4.4.4 Radionuclides

Pb-210: Produced waters from Emeline Pass exhibited a four-fold increase in Pb-210 activities (from 1.13 to 4.35 dpm·l⁻¹) between the first sample in April 1989 to the last in November 1989 (Table C.9). These Pb-210 radioactivities were 11 to 44 times higher than natural waters.

Radium: Produced waters from Emeline Pass exhibited a 35% decrease in total radium activities (from 662 to 415 dpm·l⁻¹) between the first sample period in April 1989 to the last in November 1989 (Table C.9). These total radium radioactivities are 207 to 331 times higher than natural waters.

4.5 Eugene Island

The produced water discharge from the Eugene Island (EI) Block 18 platform was sampled twice: May 1989 and November 1989.

4.5.1 Salinity and Sulfides

The Eugene Island Block 18 discharge averaged 142 ppt salinity (Table C.1). The single discharge sample analyzed for sulfides indicated no detectable amounts (Table C.1).

4.5.2 Organic Composition

The volatile fraction consisted mainly of benzene and toluene at 96% of the total (Figure 4.17 and Table C.6). The identified volatiles represented 97% of the total volatiles in EI produced water. The acid-extractable fraction contained 90% aromatic and aliphatic acids, while the resolved saturated hydrocarbons comprised 50% of the total saturated hydrocarbons. Naphthalene and alkyl-substituted naphthalenes were the dominant PAH detected in EI water, comprising 92% of the total PAH (Figure 4.17 and Table C.7). Between sampling periods there were only slight changes in concentration of all organics with the exception of the aliphatic acids. The total daily output of PAH by the Eugene Island platform was estimated to be 1.4 kg (see Section 4.9).

4.5.3 Trace Metals

The discharges from the Eugene Island platform contained high concentrations of Ba (Figure 4.16 and Table C.8). The levels of Ba were 10 times greater than V, the next highest in concentration. Ni, Zn and Cu were several orders of magnitude greater than Cd and Pb, with Hg

not detected. There were no significant variations in metal concentration between the two sample periods.

4.5.4 Radionuclides

Pb-210: Produced waters from the Eugene Island platform had Pb-210 radioactivities ranging from 3.71 to 5.21 dpm·l⁻¹ for the two sample periods (May and November 1989) (Table C.9). These Pb-210 activities are 37 to 52 times higher than natural waters.

Radium: Produced waters from the Eugene Island platform had total radium radioactivities ranging from 1232 to 1394 dpm·l⁻¹ for the two sample periods (May and November 1989) (Table C.9). These total radium activities are 616 to 697 times higher than natural waters.

4.6 East Timbalier Island

Two produced water discharges were sampled once in the East Timbalier Island study area: T-1 (Tank Battery 21, 27, 28) and T-2 (Tank Battery 36, 37). The discharge at Tank Battery 35 had been discontinued long before the field studies. No State-generated produced water discharges were sampled.

4.6.1 Salinity and Sulfides

The two discharges were similar in salinity: 154 ppt for T-1 and 158 ppt for T-2 (Table C.1). No analyses were conducted for sulfides.

4.6.2 Organic Composition

The volatile fraction from both discharges contained 94% benzene and toluene, with the T-1 water having almost four times more total volatiles than T-2 (Figure 4.18 and Table C.6). The acid-extractable fractions contained 95% acids for T-2 and 85% for T-1, with phenols in T-1 water three times higher than in T-2. The total saturated hydrocarbons in T-1 was twice that of T-2, with the resolved component being 56% for T-1 versus 50% for T-2. Although there were large differences between discharges in the amounts of volatiles, phenols and saturated hydrocarbons, the PAH fraction from these discharges was very similar (Figure 4.15 and Table C.7). The T-1 discharge had slightly higher amounts of naphthalenes, however, the other PAH were almost equal in concentration. The distribution of PAH was the same for both discharges with naphthalenes comprising 78% of the total. Despite similar PAH content of the two discharges, the daily estimated discharge of PAH for T-1 was much higher than T-2 (2.0 kg versus 0.6 kg) because of the higher daily discharge rate for T-1.

4.6.3 Trace Metals

Ba was the metal in highest concentration in the two discharges from the East Timbalier Island study area (Figure 4.19 and Table C.8). Ba concentrations were 15 to 20 times higher than V. Other metals detected in both discharge samples (in order of decreasing concentration) were Ni, Zn, Cu, Cr, Cd and Pb. The concentrations of all metals, with the exception of Ba, were similar.

4.6.4 Radionuclides

Pb-210: Produced waters from the two discharges at the East Timbalier Island area (T-1 and T-2) had Pb-210 radioactivities of 7.58 and 10.51 dpm·l⁻¹, respectively (Table C.9). These Pb-210 activities are 76 to 105 times higher than natural waters.

Radium: Produced waters from the two discharges at the East Timbalier Island area (T-1 and T-2) had total radium radioactivities of 1462 and 1299 $\text{dpm}\cdot\text{l}^{-1}$, respectively (Table C.9). These total radium activities are 731 and 650 times higher than natural waters.

4.7 Romere Pass

The Romere Pass study area contained two discharges of which one was OCS-generated (RP-1 OCS). The second discharge was generated in State waters (RP-2 State).

4.7.1 Salinity and Sulfides

The salinities for the two discharges in Romere Pass were different: 43 ppt for RP-1 OCS and 98 ppt for RP-2 State (Table C.1). The sulfide concentrations were also considerably different: $48.0\ \mu\text{g-at S}\cdot\text{l}^{-1}$ for RP-1 OCS and $3.6\ \mu\text{g-at S}\cdot\text{l}^{-1}$ for RP-2 State (Table C.1).

4.7.1 Organic Composition

The discharge from RP-1 OCS contained mostly benzene and toluene (84%) in the identified portion, with identified volatiles being 75% of the total load (Figure 4.20 and Table C.6). The volatile content of RP-2 State was complex, with the identified hydrocarbons accounting for only 30% of the estimated total volatiles. A homologous series of saturated hydrocarbons was noted that would account for another 20%. The remaining 50% of volatile hydrocarbons not identified is probably comprised of some of the compounds outlined in Section 3.5.5. The RP-1 OCS discharge water contained more acids than RP-2 State, however, the amounts of phenols were about equal. Saturated hydrocarbon levels were about the same for these discharges, with RP-2 State having a slightly larger resolved component. The PAH fraction contained naphthalenes at 81% for RP-1 OCS and 87% for RP-2 State, with C3-naphthalenes being the dominant compound (Figure 4.20 and Table C.7). The total daily output of PAH by the two discharges at Romere Pass was 0.4 kg for RP-1 OCS and 3.0 kg for RP-2 State (see Section 4.9).

4.7.3 Trace Metals

The two discharges from the Romere Pass study area differed in the distribution of the metals detected (Figure 4.19 and Table C.8). Ba was in highest concentration in RP-1 OCS, while V was highest in RP-2 State. The concentrations of Ni, Cu, Cr and Zn were at similar levels in both discharges. Cd, Hg and Pb were detected in RP-1 OCS, but not in RP-2 State.

4.7.4 Radionuclides

Pb-210: Produced waters from the two discharges at Romere Pass (RP-1 OCS and RP-2 State) had Pb-210 radioactivities of 1.53 and 1.88 $\text{dpm}\cdot\text{l}^{-1}$, respectively (Table C.9). These Pb-210 activities are 15 to 19 times higher than natural waters.

Radium: Produced waters from the two discharges at Romere Pass (RP-1 OCS and RP-2 State) had total radium radioactivities of 231 and 867 $\text{dpm}\cdot\text{l}^{-1}$, respectively (Table C.9). These total radium activities are 116 to 434 times higher than natural waters.

4.8 Empire Waterway

4.8.1 Salinity and Sulfides

The salinity of the discharge was 140 ppt and the sulfide concentration was $6.5\ \mu\text{g-at S}\cdot\text{l}^{-1}$ (Table C.1).

4.8.2 Organic Composition

Benzene and toluene comprised 83% of identified volatiles in the EW water (Figure 4.21 and Table C.6). The acid-extractable fraction contained 96% aromatic and aliphatic acids, while resolved hydrocarbons comprised 42% of the total saturated hydrocarbons. Naphthalenes were 80% of the total PAH, with phenanthrenes at 11% (Figure 4.21 and Table C.7). The daily discharge of PAH by the Empire Waterway facility was estimated at 0.9 kg (see Section 4.9).

4.8.3 Trace Metals

The Empire Waterway discharge water sample contained V, Ni and Ba in highest concentration (Figure 4.19 and Table C.8). V was almost three times higher in concentration than both Ni and Ba. Cu, Cr and Zn were next highest in concentration, followed by Cd and Pb. Hg was not detected.

4.8.4 Radionuclides

Pb-210: Produced waters from the Empire Waterway discharge had a Pb-210 radioactivity of $1.56 \text{ dpm}\cdot\text{l}^{-1}$ (Table C.9), about 16 times higher than natural waters.

Radium: Produced waters from the Empire Waterway discharge had a total radium radioactivity of $1996 \text{ dpm}\cdot\text{l}^{-1}$ (Table C.9), about 1000 times higher than natural waters.

4.9 Comparison of Effluents

4.9.1 Salinity and Sulfides

Produced waters analyzed in the study ranged between 43 and 192 ppt salinity which is within the range of 3 to 300 ppt reported by Rittenhouse et al. (1969). There was little variation in the salinity of the produced water discharge through time for those effluents sampled two or four times. Sulfide concentrations were high ($120 \mu\text{g-at S}\cdot\text{l}^{-1}$) in one of the discharges and elevated in several others (3.6 to $48 \mu\text{g-at S}\cdot\text{l}^{-1}$). The remaining discharges were trace or not detected. Where elevated levels were detected, the analyses were consistent across time for those discharges sampled more than once.

4.9.2 Hydrocarbons

The twelve produced water discharges studied here varied greatly in the amounts of organic compounds that were identified. The variations in concentrations of organics in effluents are likely the result of differences in treatment processes, efficiency of separation and the product that is being treated. The majority of the OCS treatment facilities process oil and water mixtures from a variety of platforms, which in turn obtain oil from a variety of formations. Therefore, facilities that may be using similar treatment technologies are probably treating changing input sources over time, which produces effluents of differing characteristics. It is clear from the data from several sample periods that the amounts and distribution of organic compounds can vary from the same facility over time.

The largest components of the organic load of these produced waters were the aliphatic fatty acids and the aromatic acids (Figure 4.22). The acid-extractable compounds are very water soluble and not readily sorbed onto particulate matter (Boesch and Rabalais 1987). Therefore, these compounds are less likely to be deposited in sediments, but are more likely to be diluted in the water column and dispersed from the discharge point. The saturated hydrocarbons were found to be next highest in concentration, but these compounds are the least toxic fraction of crude oil and very susceptible to microbial degradation when deposited in the environment

(National Research Council 1985, Boesch and Rabalais 1987). The volatile hydrocarbons and phenols are highly water soluble and are acutely toxic to organisms exposed to high concentrations (National Research Council 1985, Boesch and Rabalais 1987). Their long-term fate, however, is probably similar to the acids, to be diluted and dispersed in the water column.

The PAH were found to be the smallest component of these effluents, however, this fraction is the heaviest, most toxic and environmentally stable fraction of crude oil. The toxicity of crude oil is a reflection of its aromatic content, primarily the alkyl-substituted naphthalenes and phenanthrenes (National Research Council 1985, Boesch and Rabalais 1987). PAH are the most likely components of produced water discharges to be incorporated into the sediments because of low water solubilities and high sorption coefficients (Boesch and Rabalais 1987). Figure 4.23 shows the distribution of PAH in the 12 produced water samples analyzed. The highest PAH component in all samples was the naphthalenes followed by the phenanthrenes, fluorenes and dibenzothiophenes. The EP discharge contained the highest amounts of all types of PAH, over twice as much as RP-2 State, the next most contaminated effluent. Besides PF-2 OCS and Exxon, the remaining 8 discharges contained significant concentrations of PAH, ranging from $960 \mu\text{g}\cdot\text{l}^{-1}$ (T-1) to $410 \mu\text{g}\cdot\text{l}^{-1}$ (EI). The PAH concentration of effluents is not the only criteria that can be used to compare discharges and assess their potential impact on the environment. Discharge rates are also important. Figure 4.24 compares the daily output of PAH from the produced water discharges studied with totals of all discharges given for study areas with more than one discharge. The Conoco discharge, which is part of the BR total, had the highest PAH discharge rate of any individual discharge. Of those total PAH discharge rates for any single receiving environments which had multiple discharges, the total for Bayou Rigaud was highest followed by Romere Pass.

Figures 4.25 and 4.26 compare the concentrations of benzene + toluene (volatiles) and naphthalenes ($\text{C}_0\text{-C}_3$) in 24 produced water discharges, 10 that are OCS-generated from this study and 14 State. The highest volatile concentrations reported in this study ($4,200$ to $5,600 \mu\text{g}\cdot\text{l}^{-1}$) were only lower than three discharges reported in the literature ($6,800$ to $12,000 \mu\text{g}\cdot\text{l}^{-1}$). The lowest concentrations of volatiles of the 24 discharges was found in PF-2 OCS ($180 \mu\text{g}\cdot\text{l}^{-1}$). The remainder of the discharges from this study fell in a similar range as previously reported discharges (590 to $3,400 \mu\text{g}\cdot\text{l}^{-1}$). The amounts of the more environmentally persistent naphthalenes in the 24 discharges fell into three groups. Two discharges, Trinity Bay and Emeline Pass, contained naphthalenes that were twice as high as any other discharge ($1,300$ to $1,600 \mu\text{g}\cdot\text{l}^{-1}$). The second group was made up of 16 discharges that ranged from $210 \mu\text{g}\cdot\text{l}^{-1}$ to $780 \mu\text{g}\cdot\text{l}^{-1}$ of naphthalenes. The last group of 6 discharges contained naphthalenes ranging in concentration from $29 \mu\text{g}\cdot\text{l}^{-1}$ to $120 \mu\text{g}\cdot\text{l}^{-1}$. Overall the discharges from this study spanned the range of concentrations of volatiles and naphthalenes that have been observed in other studies. Data from multiple sample periods in this study show that concentrations are variable over time which somewhat limits the ability to compare discharges. Among all the 24 discharges examined, however, the volatile compound in highest concentration was benzene, and the PAH were dominated by naphthalene and its alkylated analogs.

4.9.3 Trace Metals

Figure 4.27 compares the mean concentrations of trace metals found in samples from the 12 produced water discharges of this study. The majority of the discharge samples had Ba, V and Ni in highest concentration. The samples from PF-1 OCS, RP-2 State and EW differed from the other discharges in distribution of trace metals, with V being in higher concentration than Ba. The highest concentration of Ba was detected in the T-1 discharge sample ($280,000 \mu\text{g}\cdot\text{l}^{-1}$), with T-2 and EI similar in concentration ($180,000$ vs. $190,000 \mu\text{g}\cdot\text{l}^{-1}$) and three times greater in concentration than the other discharges. Also, these three discharges contained the highest concentrations of Zn which follows the same pattern as Ba, with T-1 the highest ($4,700 \mu\text{g}\cdot\text{l}^{-1}$) followed by EI ($3,200 \mu\text{g}\cdot\text{l}^{-1}$) and T-2 ($2,500 \mu\text{g}\cdot\text{l}^{-1}$). V, Ni and Cr were highest in the EW

other discharges. Hg was detected in only three discharges. In most cases, the concentrations of all metals detected in these samples exceeded the levels normally found in freshwater and seawater by a factor of 1,000 (Forstner and Wittman 1983).

4.9.4 Radionuclides

Pb-210: Produced waters from the areas examined had Pb-210 radioactivities ranging from 0.21 (Bayou Rigaud: Conoco) to 25.4 (Pass Fourchon: PF-2 State) $\text{dpm}\cdot\text{l}^{-1}$. These Pb-210 activities are 2 to 254 times higher than natural waters. There appears to be no correlation between the Pb-210 activities of these produced waters and salinity as has been noted for Ra isotopes. Differences in Pb-210 activities in produced water may be due to differences in the suspended sediment concentrations of these waters. Pb-210 is very particle-reactive, quickly sorbing onto particle surfaces. Therefore, the settling out of particulate matter from produced waters may change the total Pb-210 activity of the water sample.

Radium: In all water samples, U-238 and Th-234 activities were below detection levels (<0.5 and <0.8 $\text{dpm}\cdot\text{l}^{-1}$, respectively). All samples were at or below the activity levels of U-238 and Th-234 in the surrounding natural waters. This lack of enhanced uranium and thorium activity indicates strongly that the high radioactivity levels associated with produced waters originate with the radium isotopes and is not supported by radioactive parents of radium which are higher in the decay chain. Total radium is the sum of Ra-226 and Ra-228 activities. The ratio of Ra-226/total Ra varies from site to site for produced waters, but in most cases the Ra-226 activity constitutes more than two-thirds of the total radium activity.

Produced waters from the sites examined had total radium radioactivities ranging from 304 (Bayou Rigaud: Conoco) to 2312 (Pass Fourchon: PF-1) $\text{dpm}\cdot\text{l}^{-1}$. These total radium activities are approximately 150 to 1150 times higher than natural waters. All discharges sampled had total radium activities which were in excess of the 111 $\text{dpm}\cdot\text{l}^{-1}$ activity designated by the EPA as hazardous waste (Reid 1983). Total radium activities of these produced waters correlated well with salinity as has been noted for other sites (Kraemer and Reid 1984) (Figure 4.28).

Kraemer and Reid (1984) measured total radium activity in samples of produced waters from Louisiana and Texas. The total radium concentration found in 41 samples of produced water from gas, oil and geothermal wells ranged from 42 to 6216 $\text{dpm}\cdot\text{l}^{-1}$ with salinities ranging from 8 to 274 ppt. Neff et al. (1989) reported analyses of produced waters from Gulf coast platforms with total radium values ranging from 1343 to 2697 $\text{dpm}\cdot\text{l}^{-1}$. Sixty-six percent of the samples tested by Kraemer and Reid (1984) exceeded the EPA hazardous waste level of 111 $\text{dpm}\cdot\text{l}^{-1}$ for total radium; all of the samples reported by Neff et al. (1989) exceeded 111 $\text{dpm}\cdot\text{l}^{-1}$.

The total radium values found in the present study (304-2312 $\text{dpm}\cdot\text{l}^{-1}$) are within the range of values observed by Kraemer and Reid (1984) and Neff et al. (1989). All samples examined in the present study had total radium concentrations which exceeded the 111 $\text{dpm}\cdot\text{l}^{-1}$ EPA hazardous waste level, and exceeded the 67 $\text{dpm}\cdot\text{l}^{-1}$ level set by the Nuclear Regulatory Commission as a maximum radioactivity level for liquid discharge from nuclear power plants to unrestricted access areas.

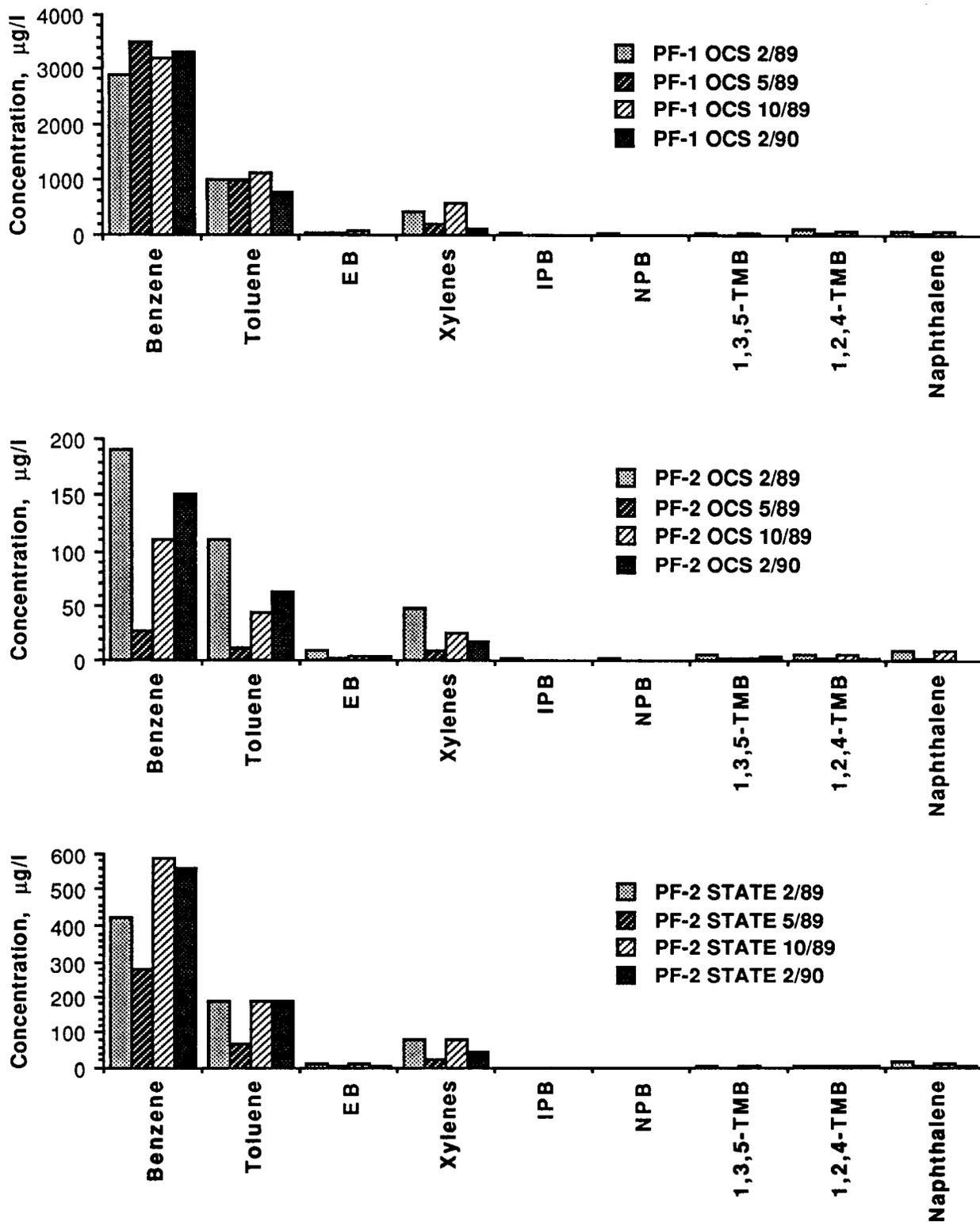


Figure 4.1 Concentrations of volatile hydrocarbons detected in Pass Fourchon produced water discharges during four sample periods. (EB=Ethylbenzene, IPB=Isopropylbenzene, NPB=n-Propylbenzene, TMB=Trimethylbenzene.)

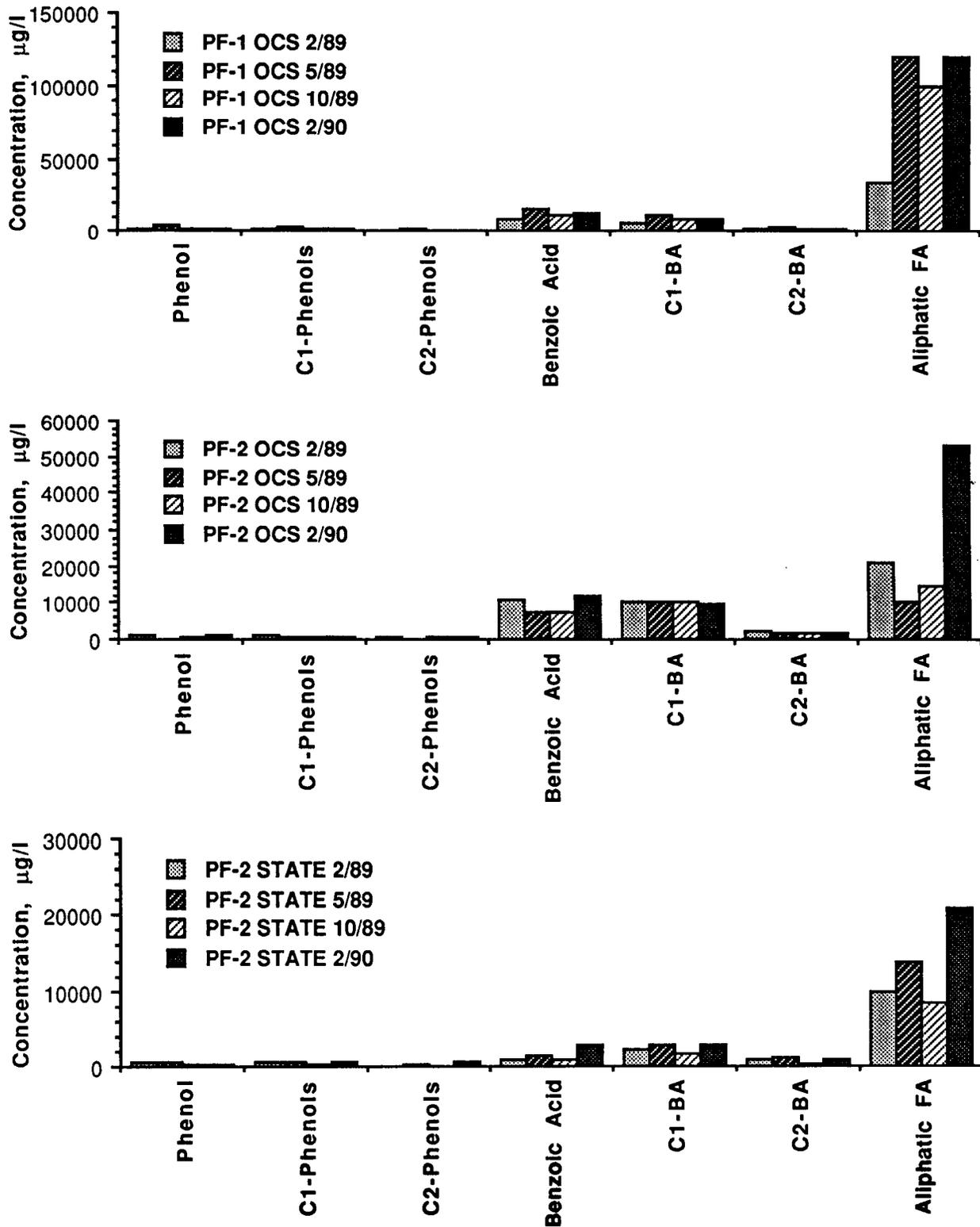


Figure 4.2. Concentrations of acid-extractable compounds detected in Pass Fourchon produced water discharges during four sample periods. (BA=Benzoic Acid, FA=Fatty Acid.)

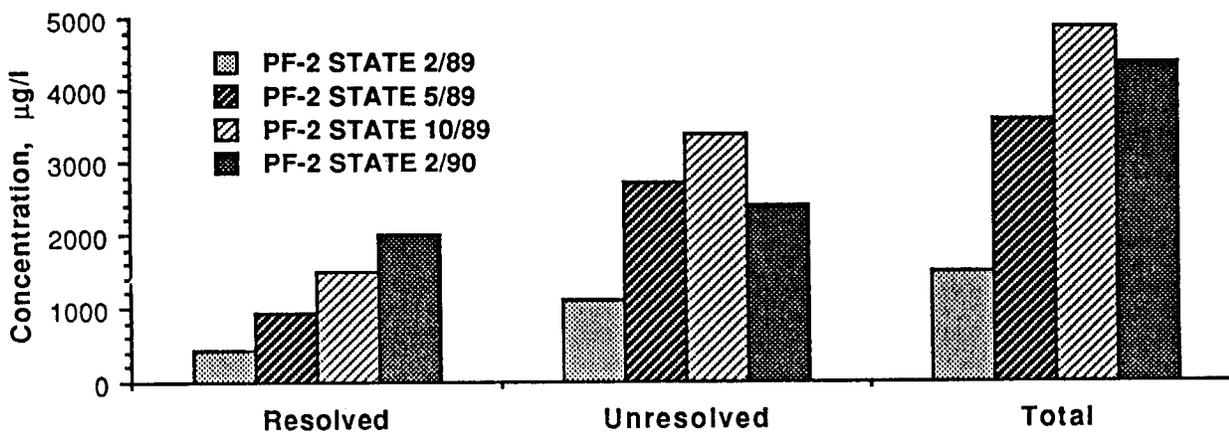
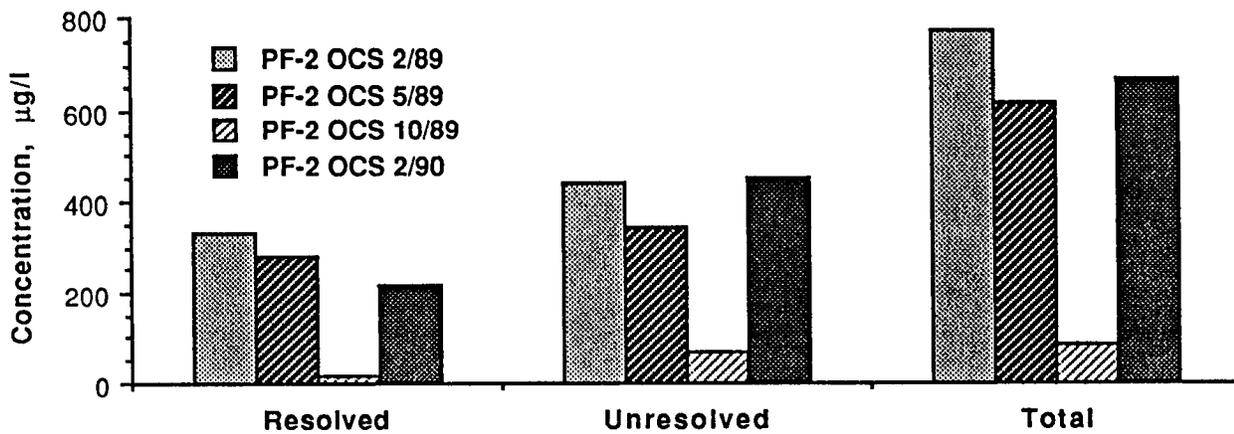
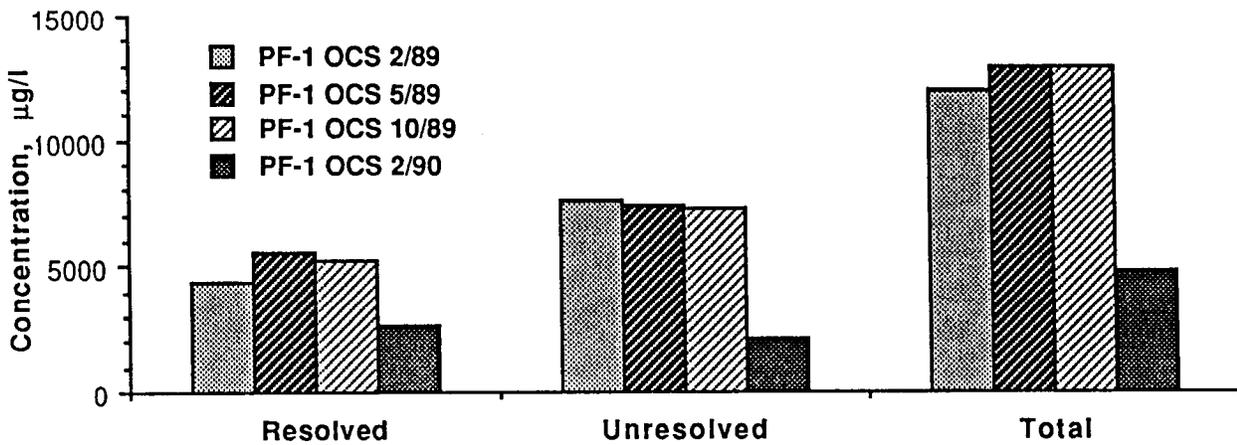


Figure 4.3. Concentrations of saturated hydrocarbons detected in Pass Fourchon produced water discharges during four sample periods.

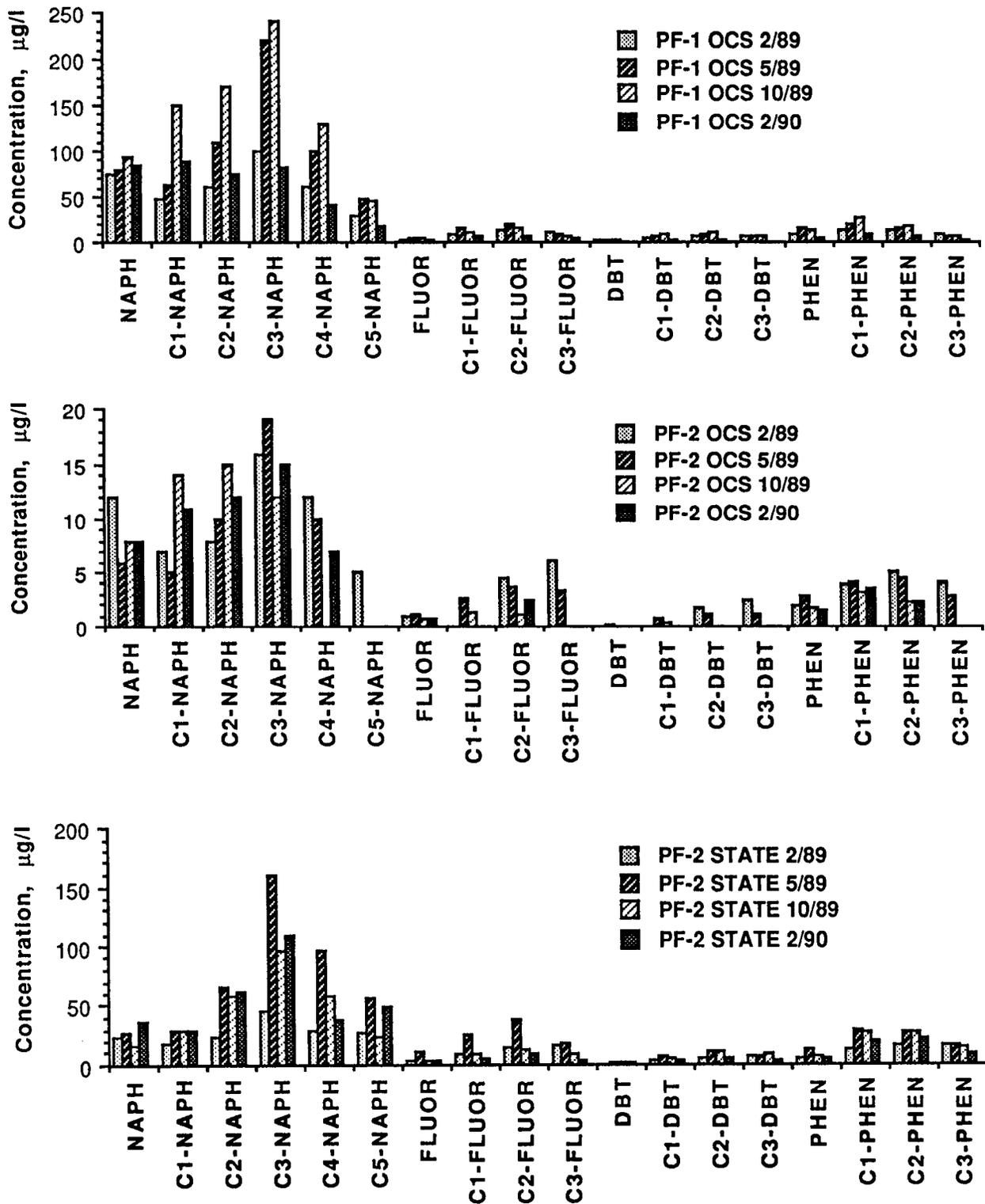


Figure 4.4. Concentrations of polynuclear aromatic hydrocarbons detected in Pass Fourchon produced water discharges during four sample periods. (NAPH=Naphthalene, FLUOR=Fluoranthene, DBT=Dibenzothiophene, PHEN=Phenanthrene.)

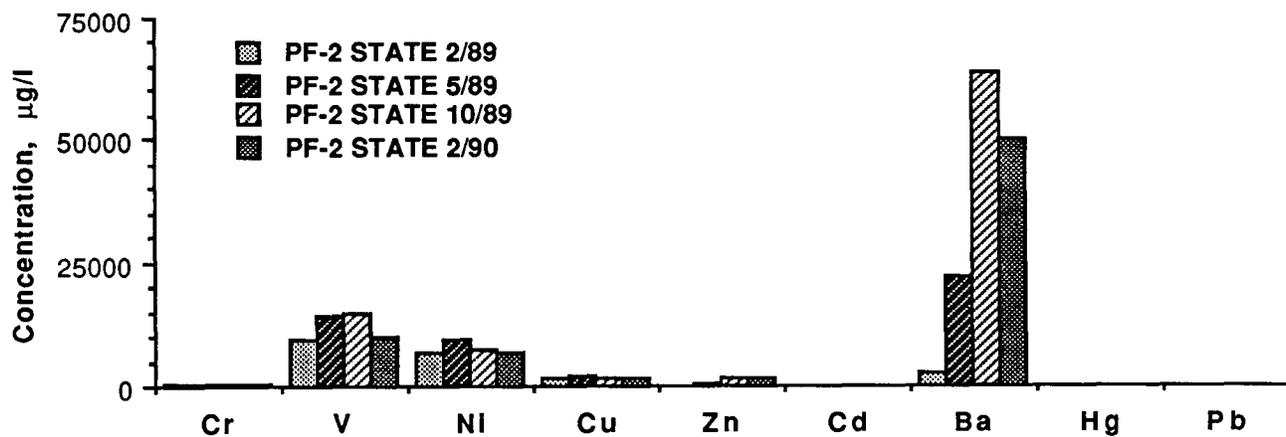
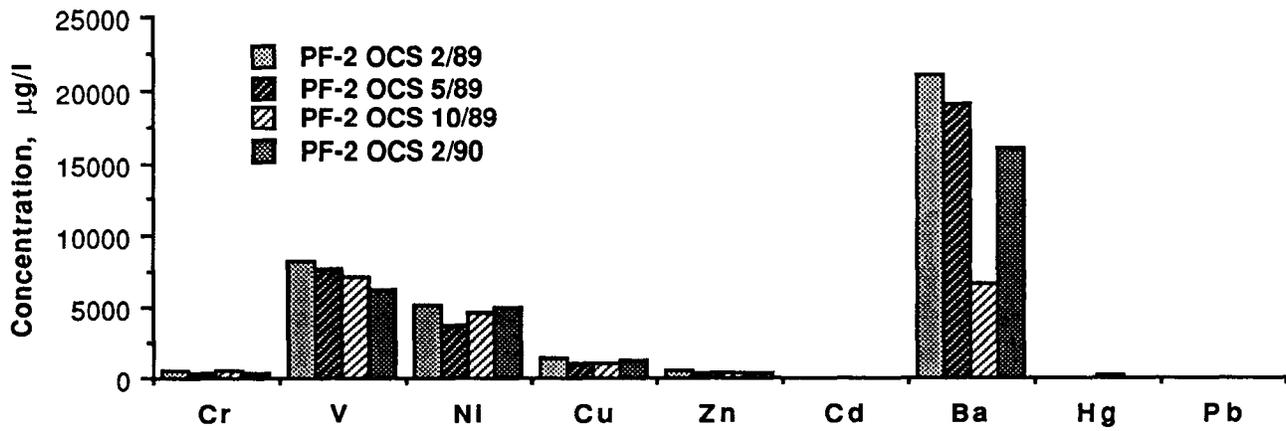
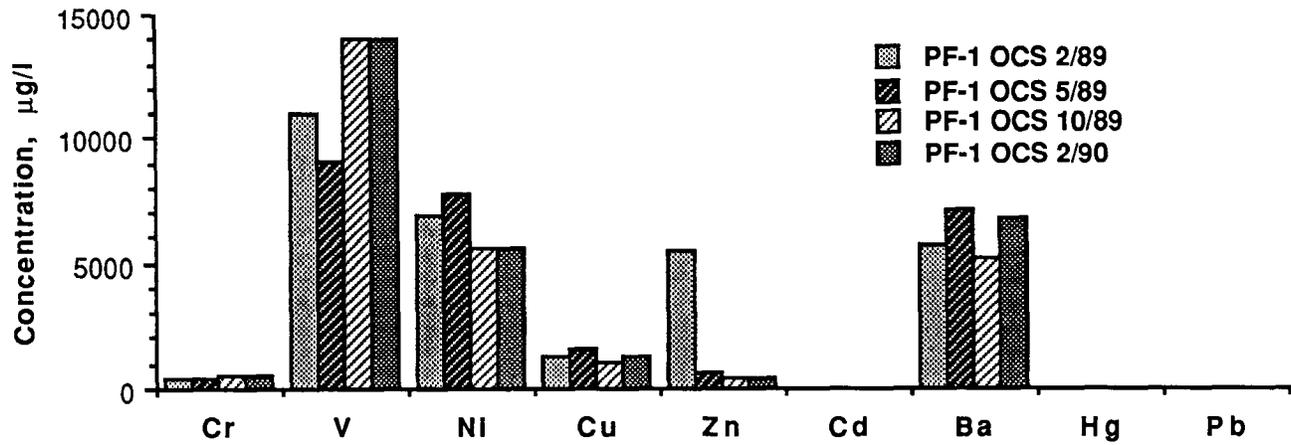


Figure 4.5. Concentrations of selected trace metals detected in Pass Fourchon produced water discharges during four sample periods.

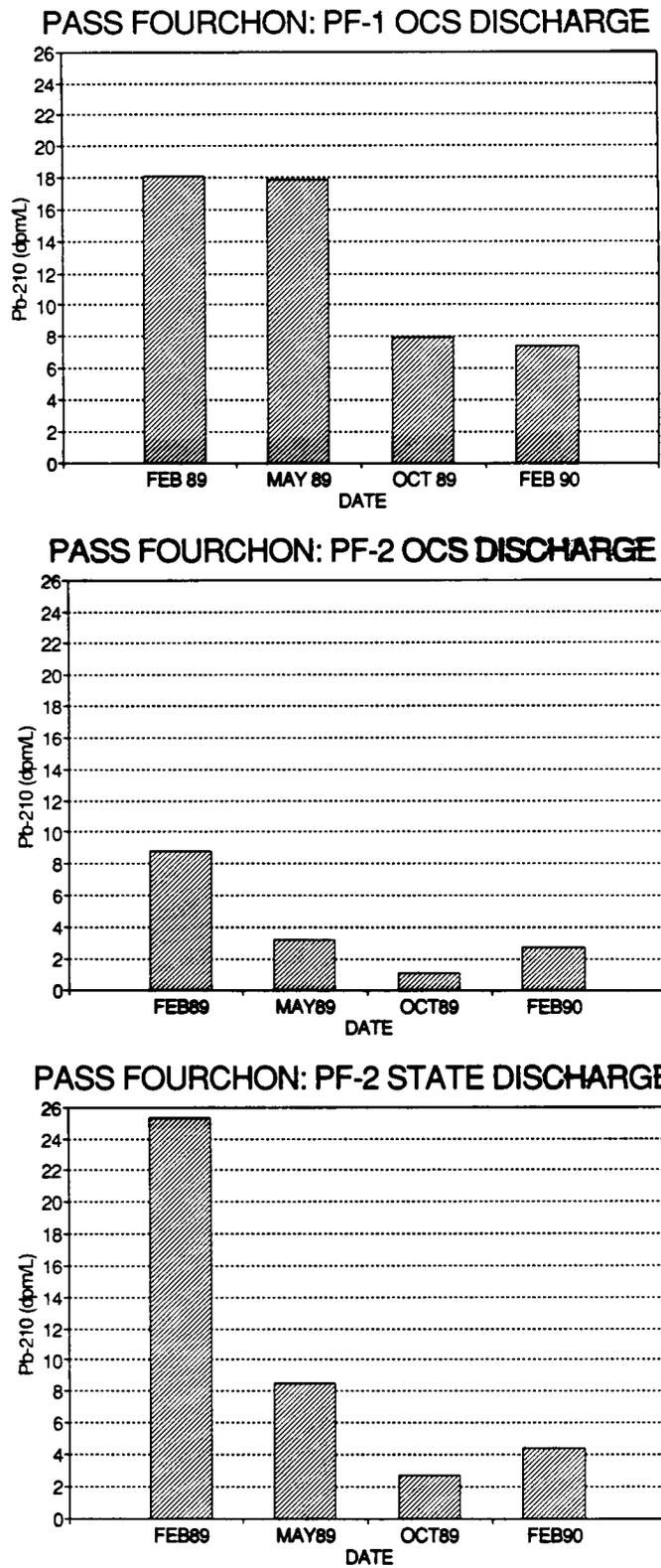


Figure 4.6. Pb-210 activity in Pass Fourchon produced water discharges during four sample periods.

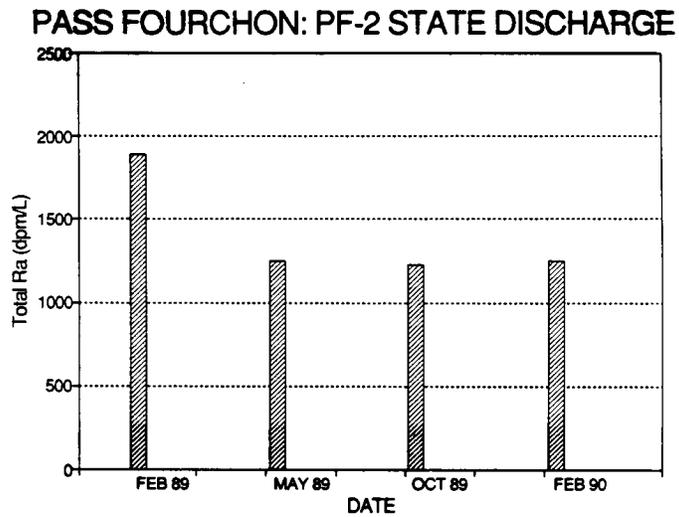
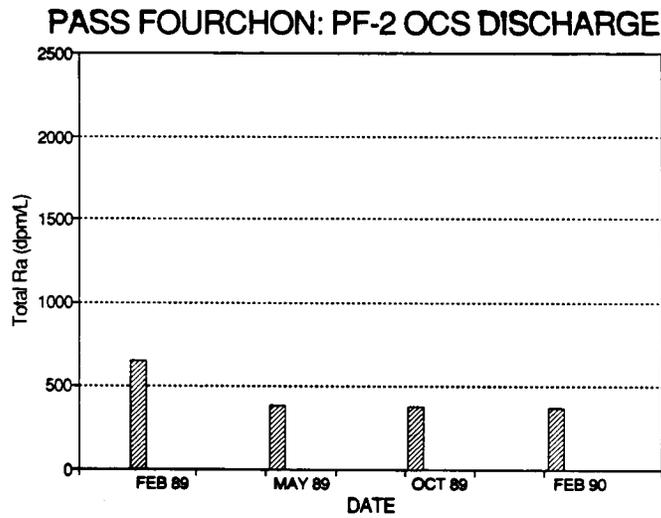
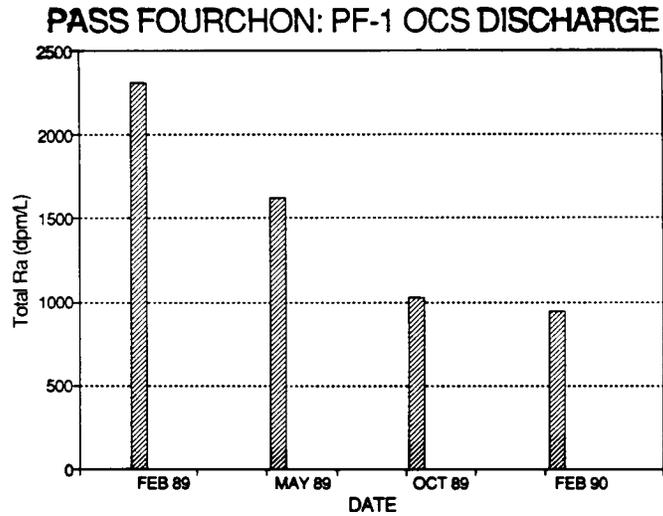


Figure 4.7. Total radium activity in Pass Fourchon produced water discharges during four sample periods.

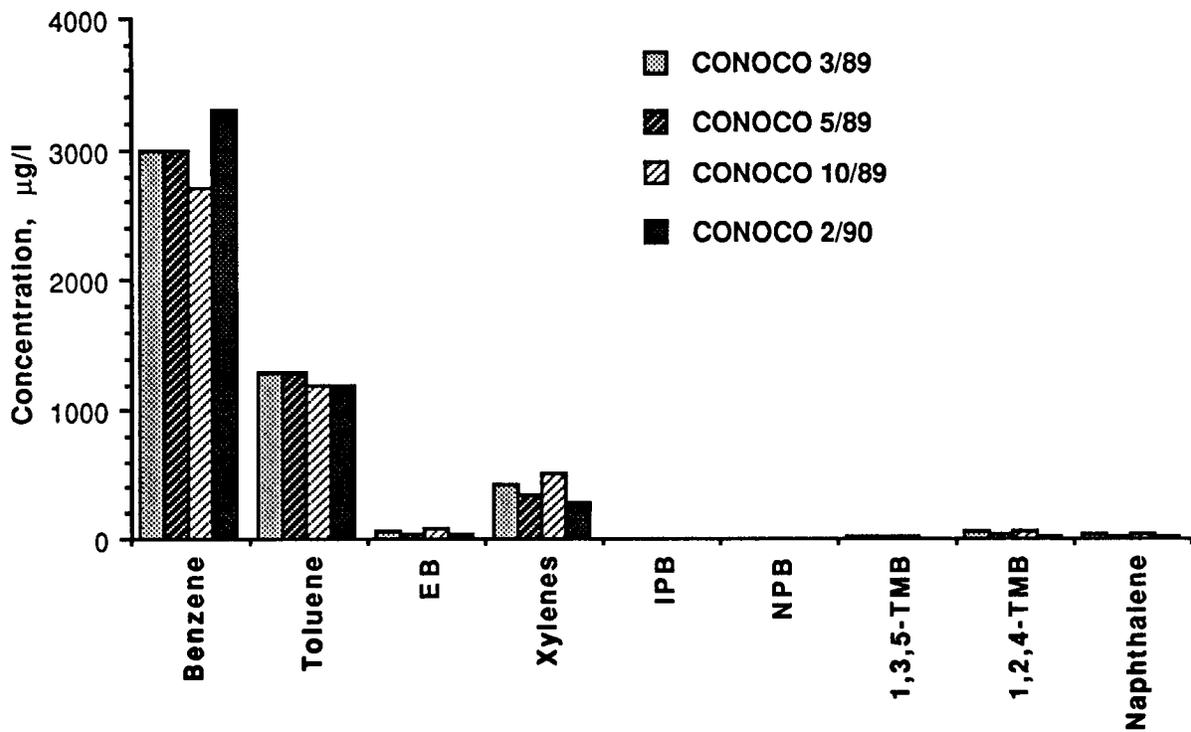
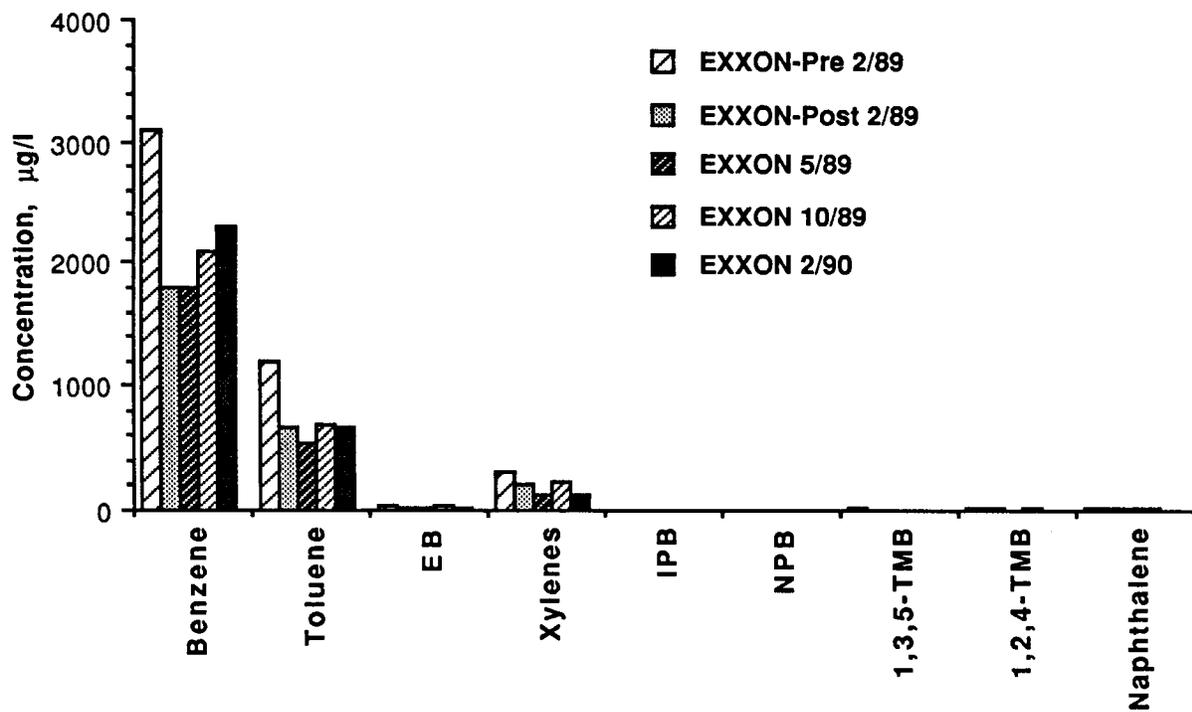


Figure 4.8. Concentrations of volatile hydrocarbons detected in Bayou Rigaud produced water discharges during four sample periods. (EB=Ethylbenzene, IPB=Isopropylbenzene, NPB=n-Propylbenzene, TMB=Trimethylbenzene.)

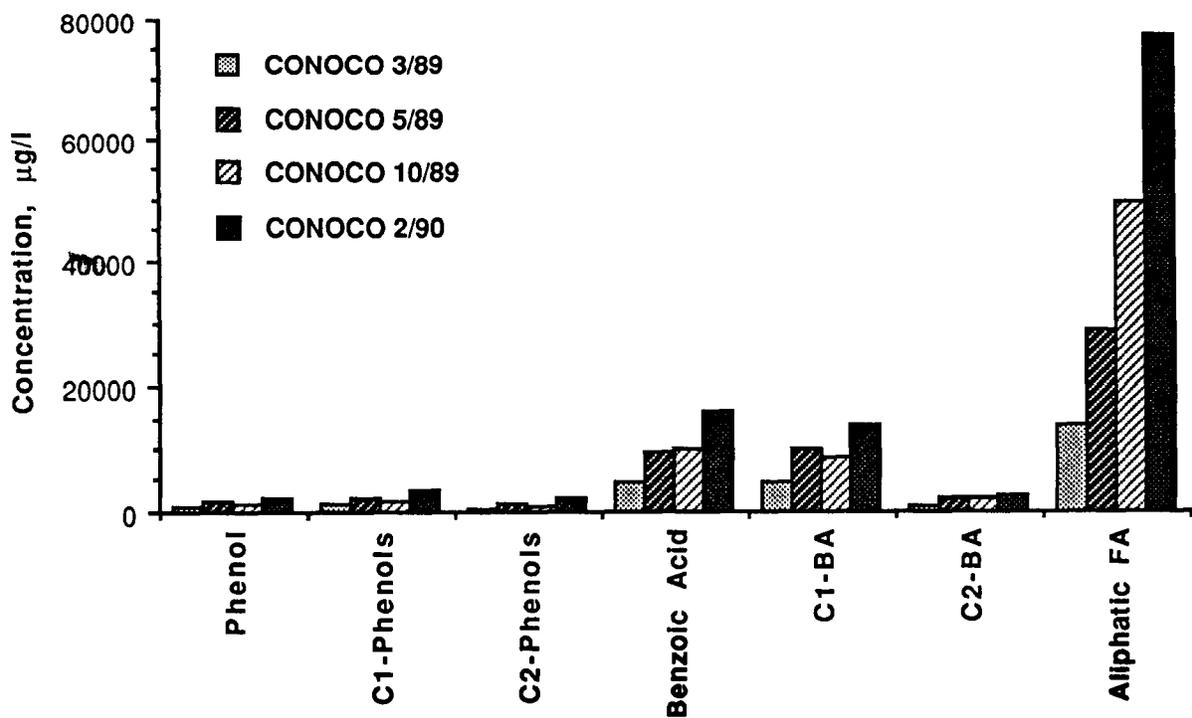
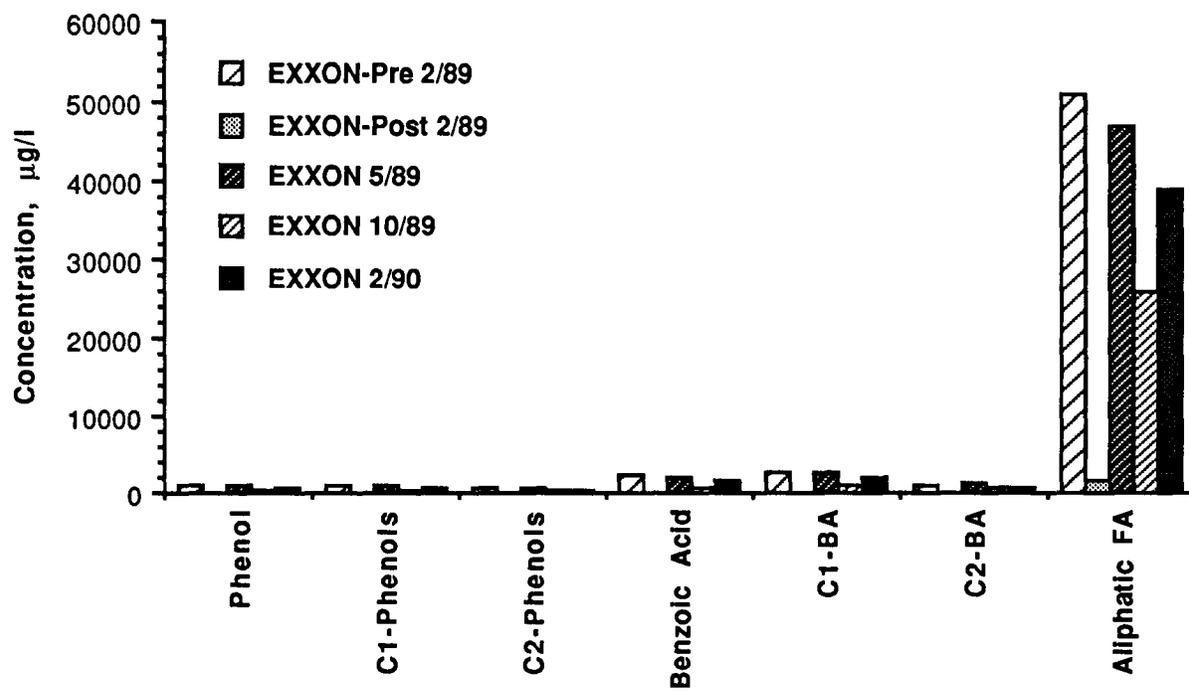


Figure 4.9. Concentrations of acid-extractable compounds detected in Bayou Rigaud produced water discharges during four sample periods. (BA=Benzoic Acid, FA=Fatty Acid.)

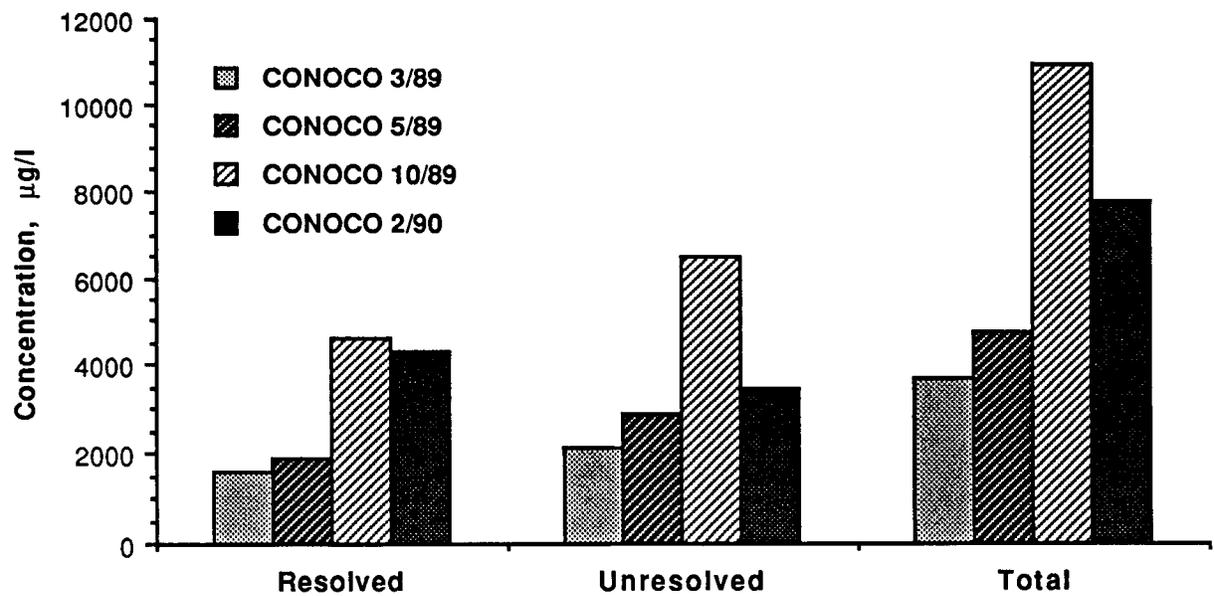
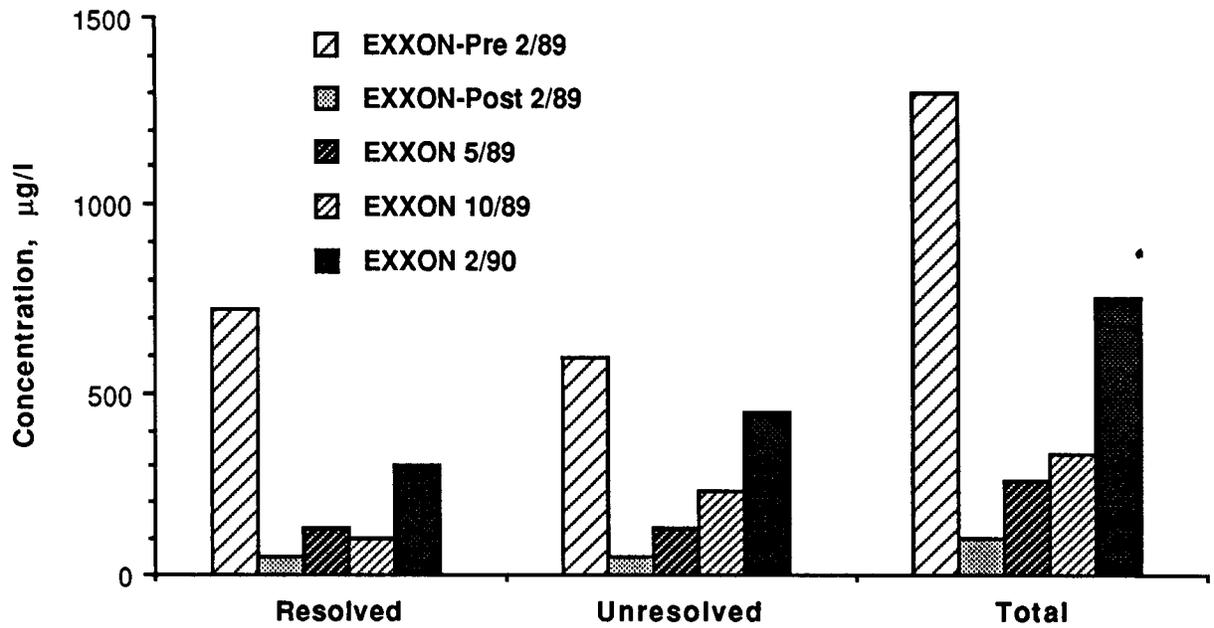


Figure 4.10. Concentrations of saturated hydrocarbons detected in Bayou Rigaud produced water discharges during four sample periods.

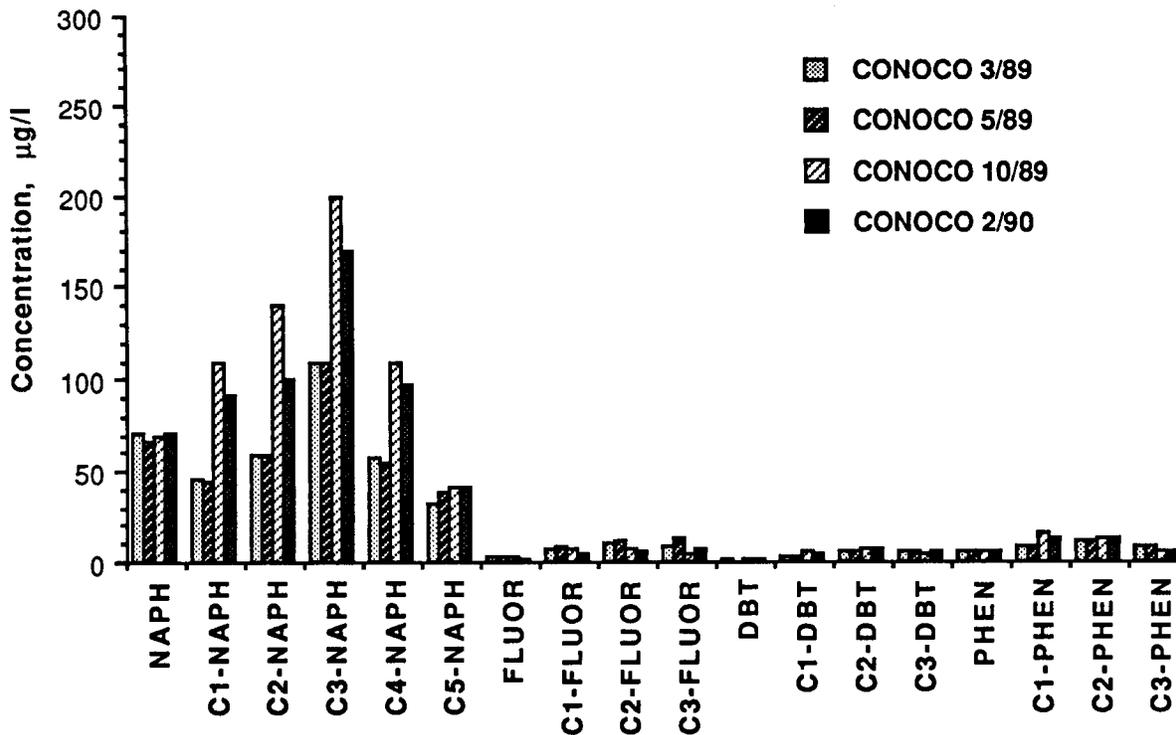
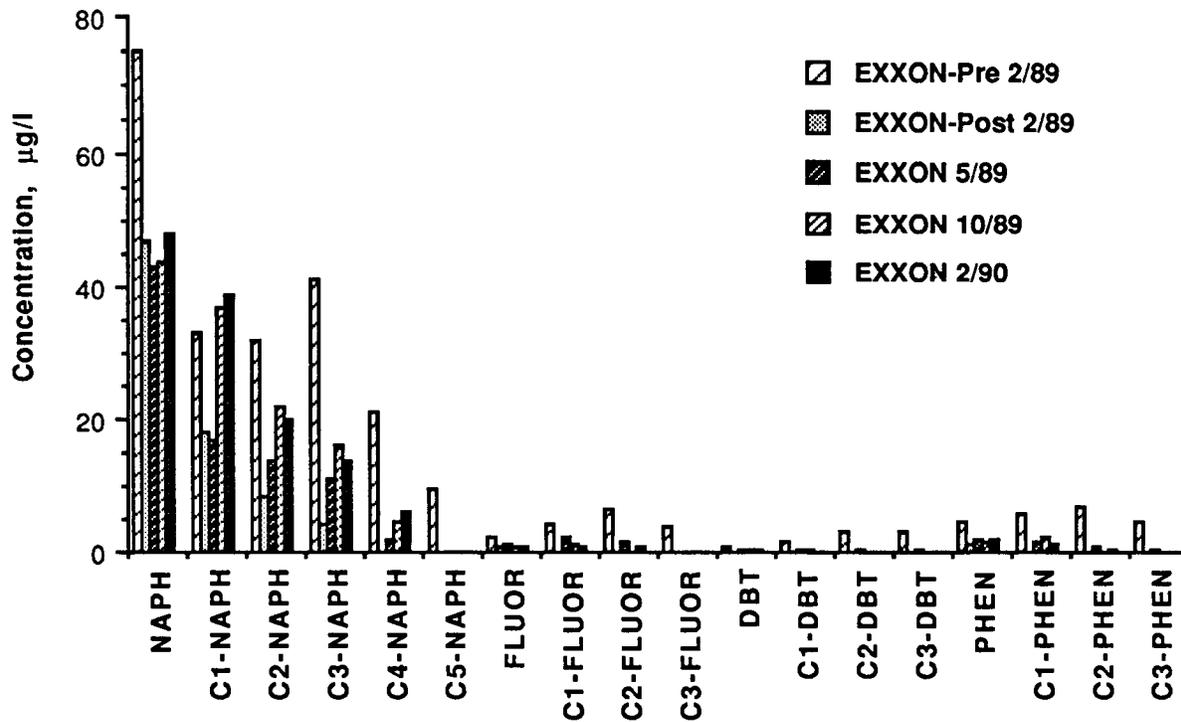


Figure 4.11. Concentrations of polynuclear aromatic hydrocarbons detected in Bayou Rigaud produced water discharges during four sample periods. (NAPH=Naphthalene, FLUOR=Fluoranthene, DBT=Dibenzothiophene, PHEN=Phenanthrene.)

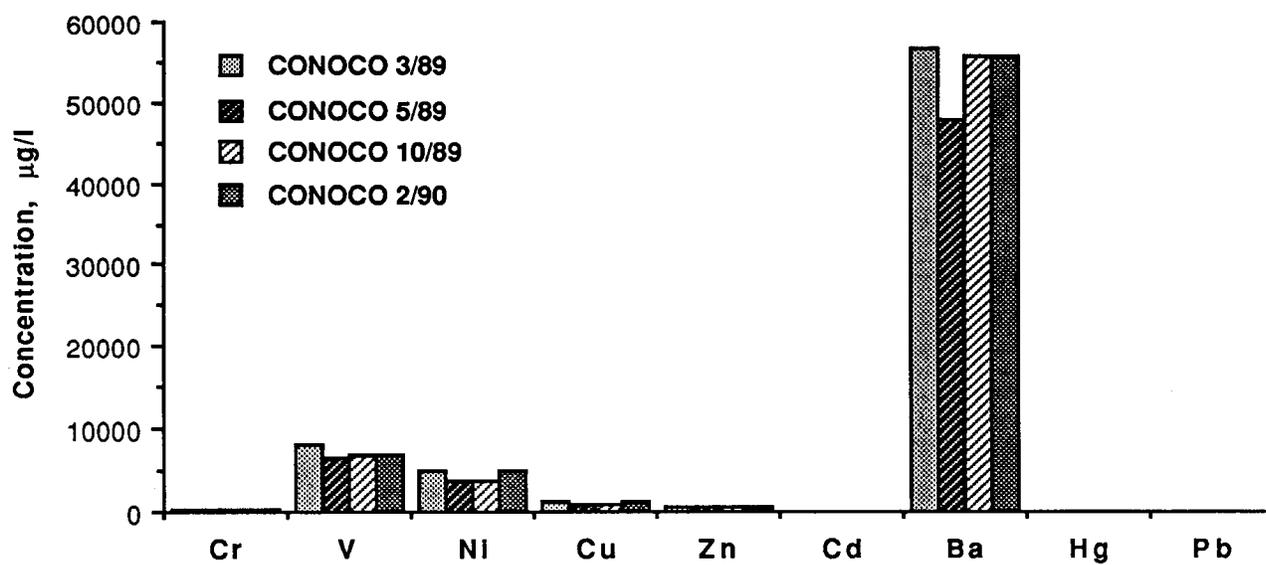
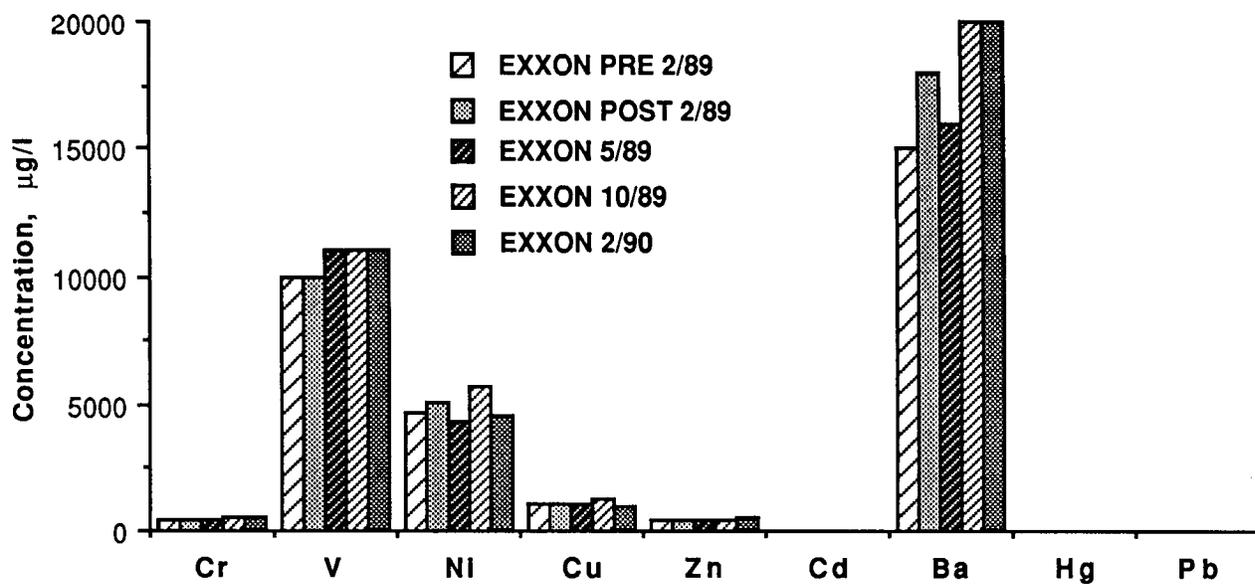
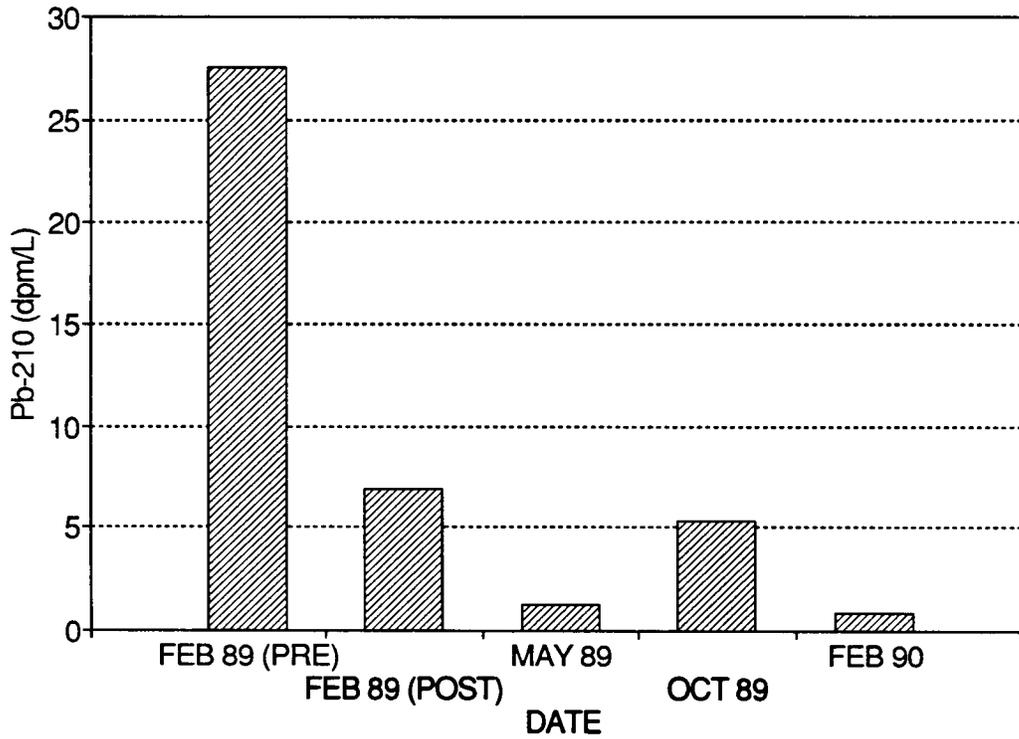


Figure 4.12. Concentration of selected trace metals detected in Bayou Rigaud produced water discharges during four sample periods.

BAYOU RIGAUD: EXXON DISCHARGE



BAYOU RIGAUD: CONOCO DISCHARGE

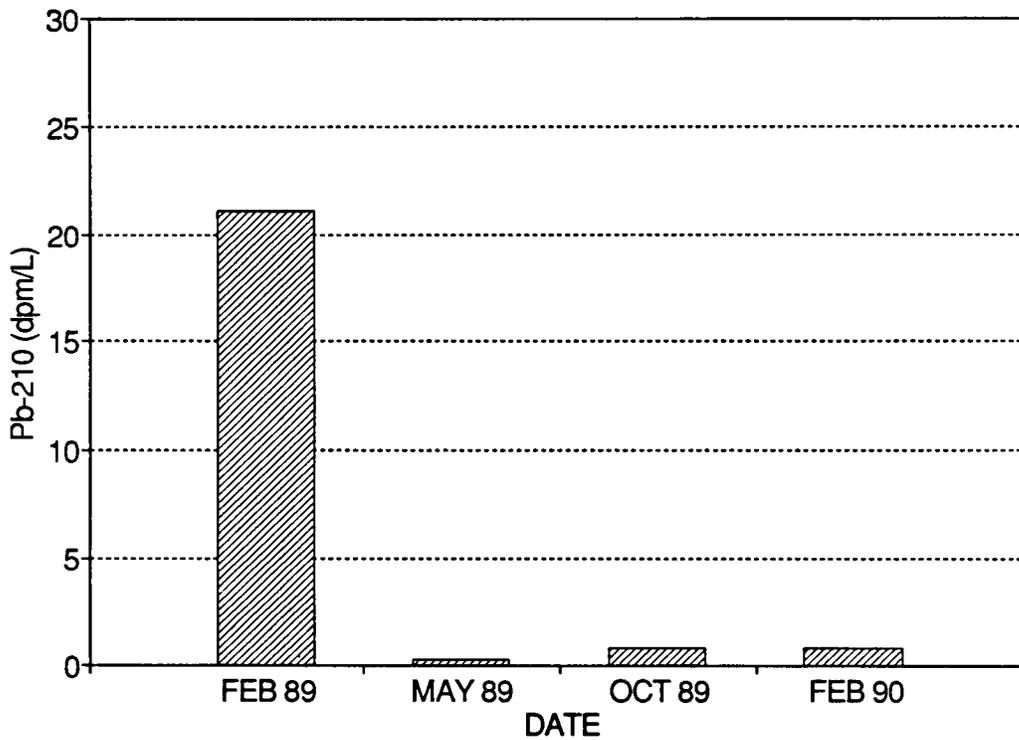
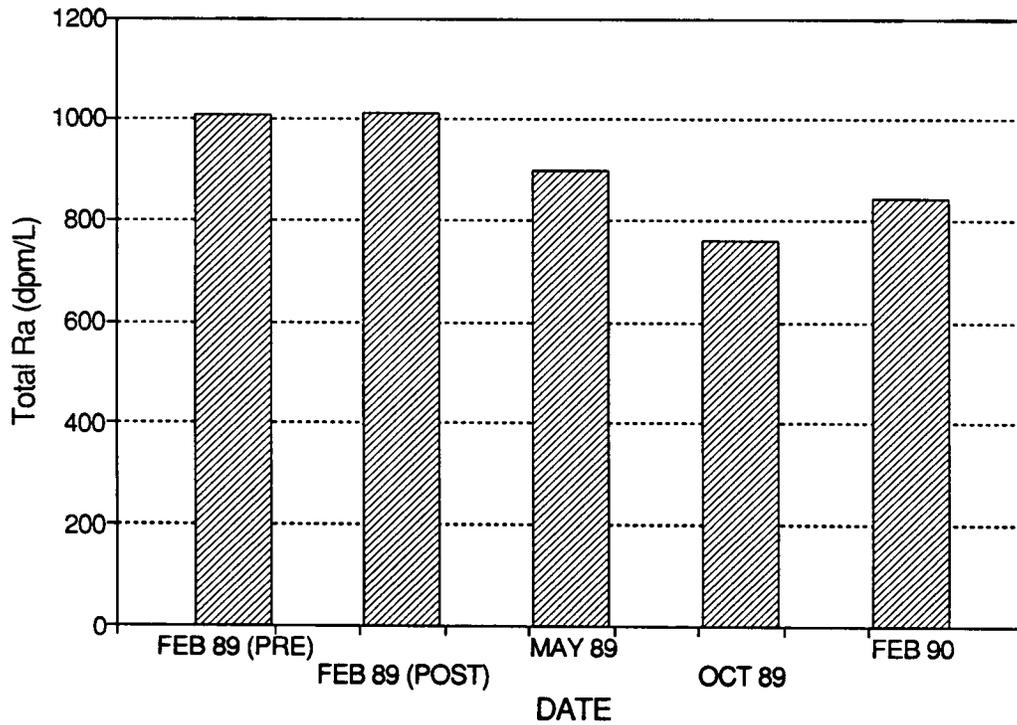


Figure 4.13. Pb-210 activity in Bayou Rigaud produced water discharges during four sample periods.

BAYOU RIGAUD: EXXON DISCHARGE



BAYOU RIGAUD: CONOCO DISCHARGE

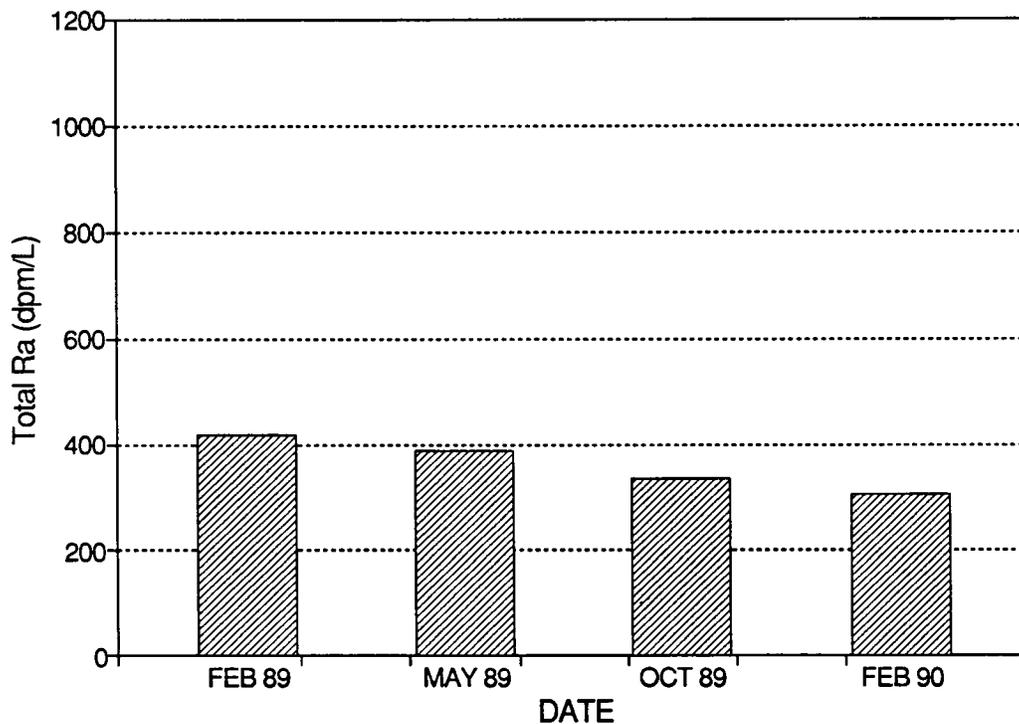


Figure 4.14. Total radium activity in Bayou Rigaud produced water discharges during four sample periods.

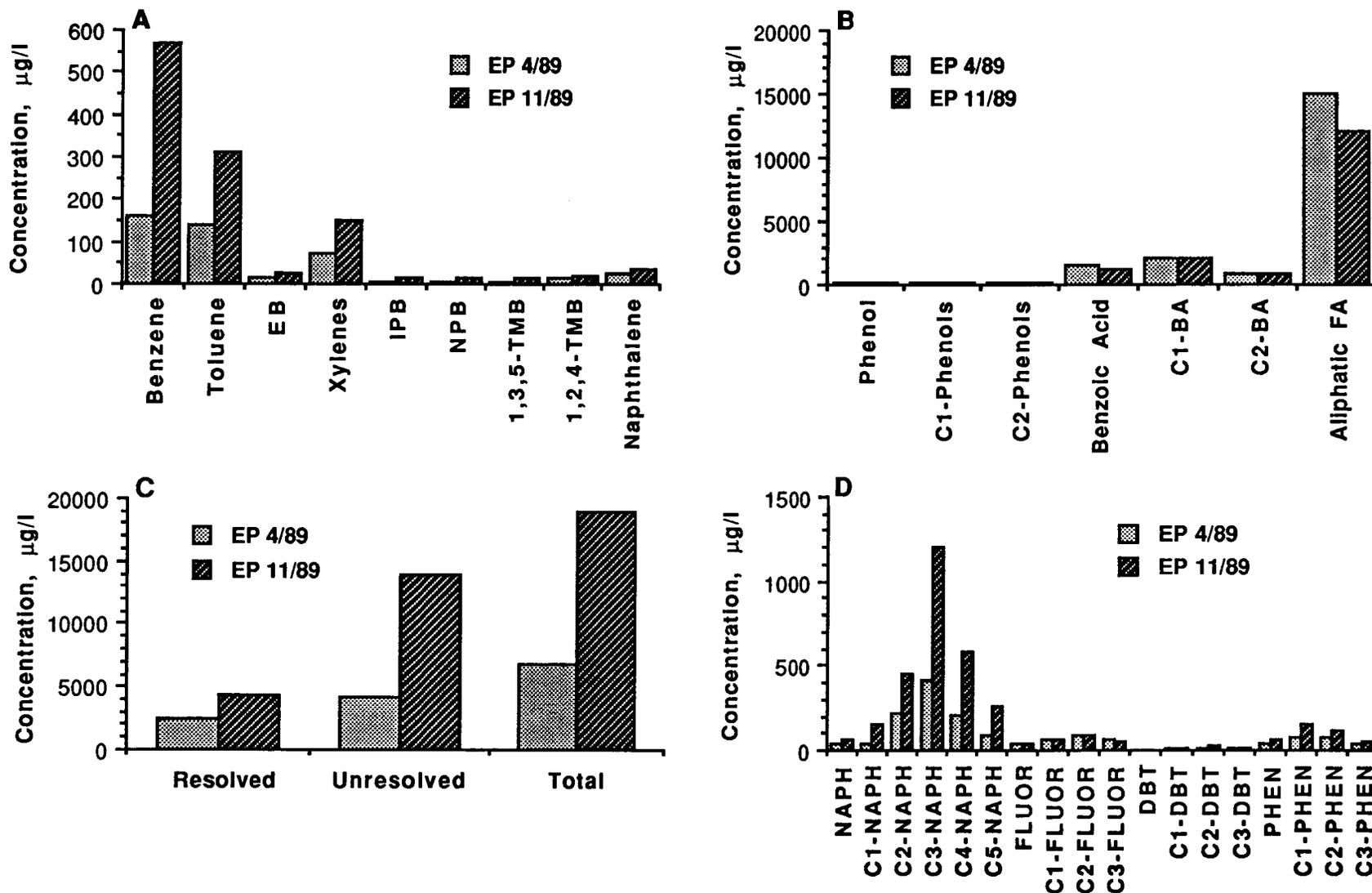


Figure 4.15. Concentrations of A) volatile hydrocarbons, B) acid-extractable compounds, C) saturated hydrocarbons and D) polynuclear aromatic hydrocarbons in the produced water discharge from Emeline Pass during two sample periods. (EB=Ethylbenzene, IPB=Isopropylbenzene, NPB=n-Propylbenzene, TMB=Trimethylbenzene, BA=Benzoic Acid, FA=Fatty Acid, NAPH=Naphthalene, FLUOR=Fluoranthene, DBT=Dibenzothiophene, PHEN=Phenanthrene.)

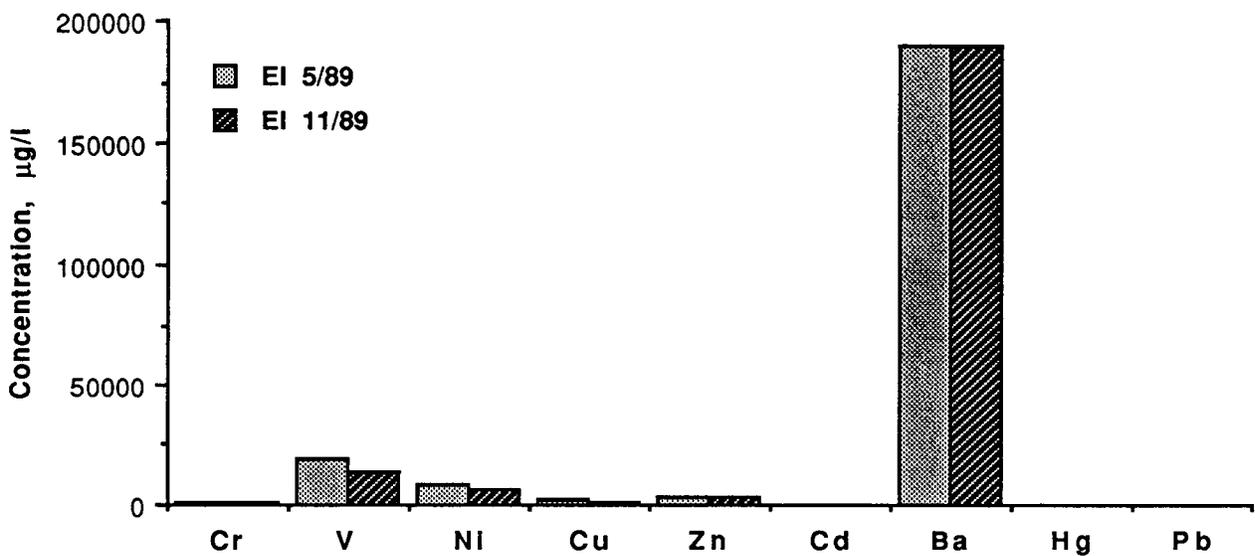
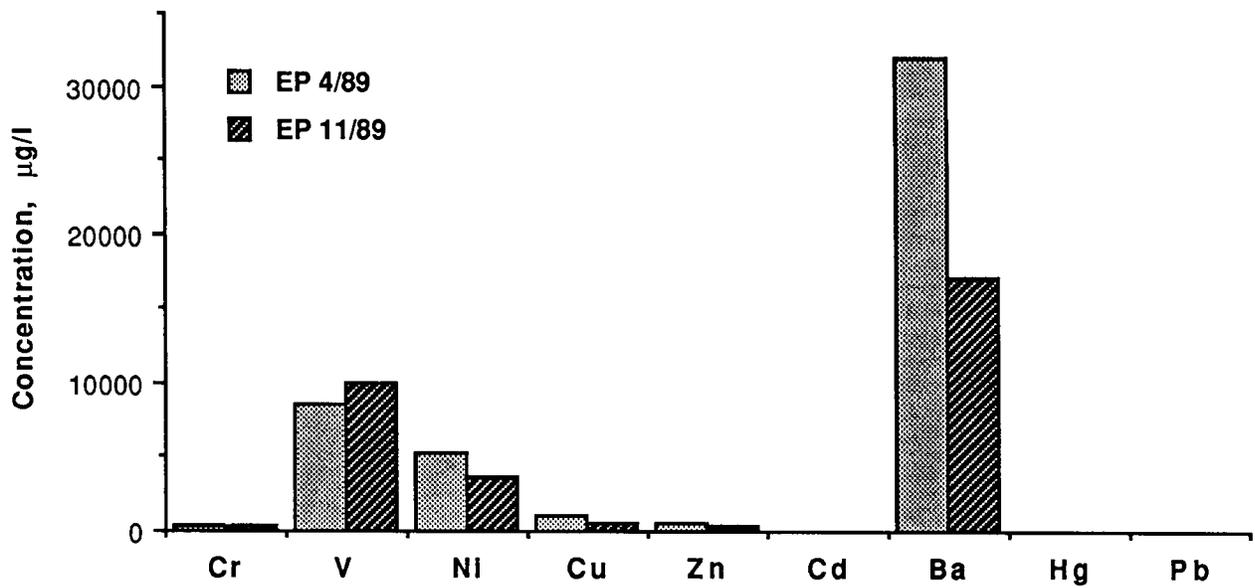


Figure 4.16. Concentration of selected trace metals detected in produced water discharges from Emeline Pass and Eugene Island during two sample periods.

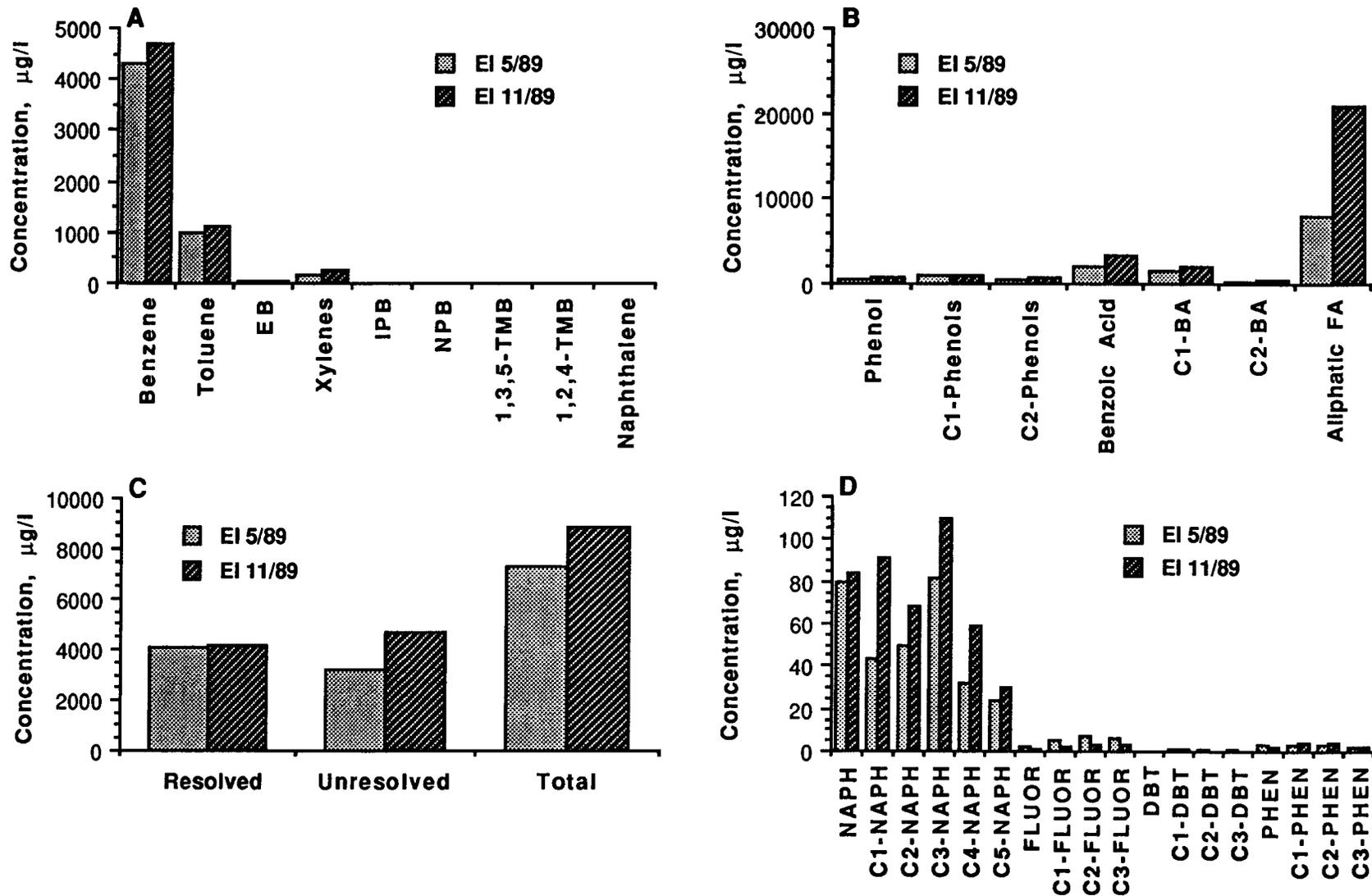


Figure 4.17. Concentrations of A) volatile hydrocarbons, B) acid-extractable compounds, C) saturated hydrocarbons and D) polynuclear aromatic hydrocarbons in the produced water discharge from Eugene Island during two sample periods. (EB=Ethylbenzene, IPB=Isopropylbenzene, NPB=n-Propylbenzene, TMB=Trimethylbenzene, BA=Benzoic Acid, FA=Fatty Acid, NAPH=Naphthalene, FLUOR=Fluoranthene, DBT=Dibenzothiophene, PHEN=Phenanthrene.)

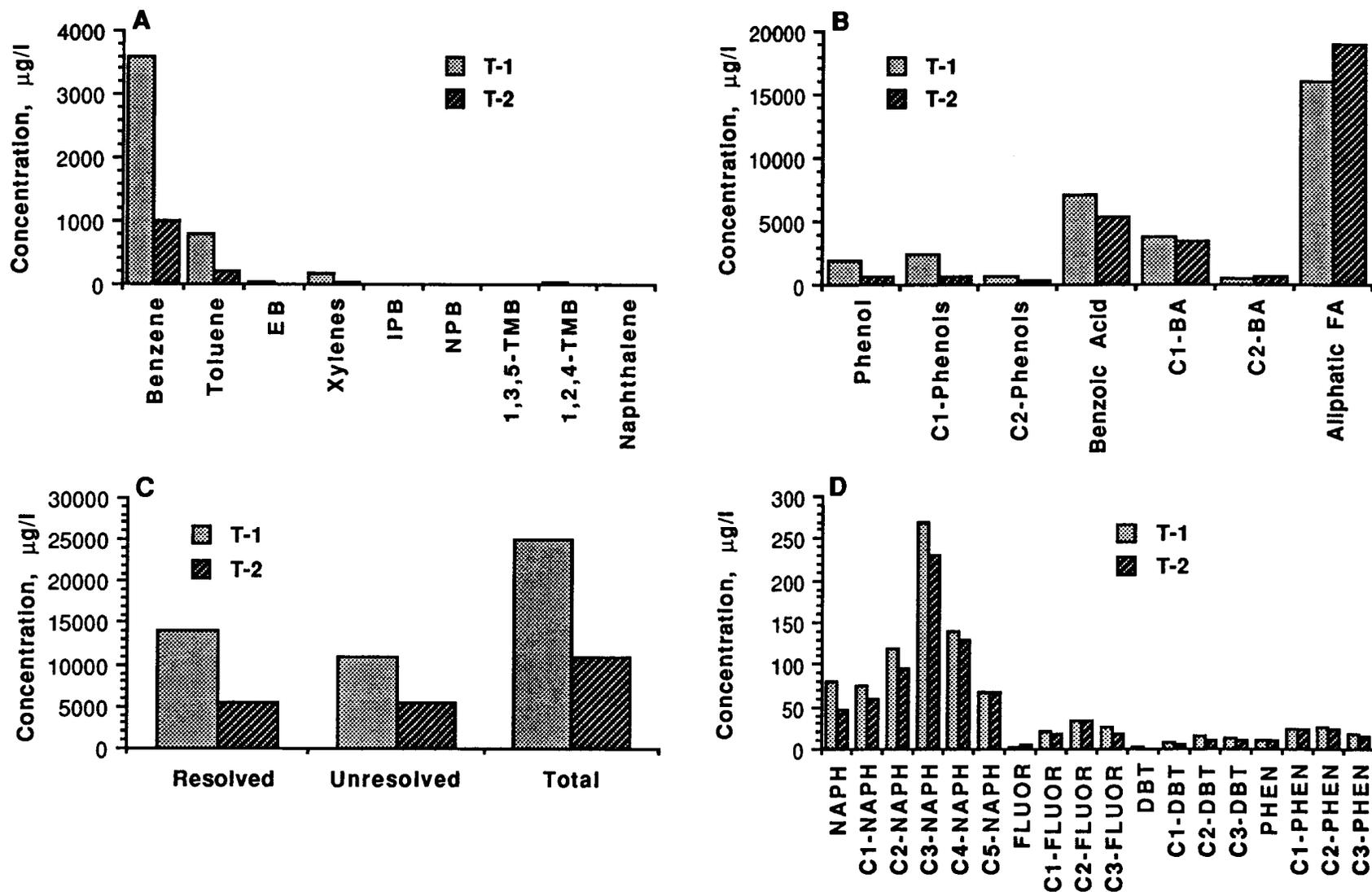


Figure 4.18. Concentrations of A) volatile hydrocarbons, B) acid-extractable compounds, C) saturated hydrocarbons and D) polynuclear aromatic hydrocarbons in the produced water discharges T-1 and T-2 from East Timbalier Island. (EB=Ethylbenzene, IPB=Isopropylbenzene, NPB=n-Propylbenzene, TMB=Trimethylbenzene, BA=Benzoic Acid, FA=Fatty Acid, NAPH=Naphthalene, FLUOR=Fluoranthene, DBT=Dibenzothiophene, PHEN=Phenanthrene.)

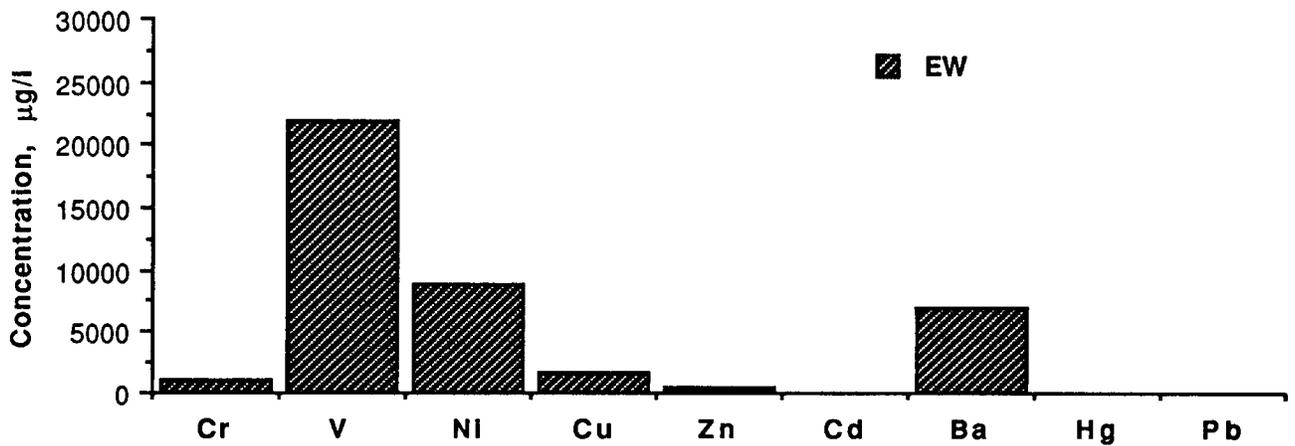
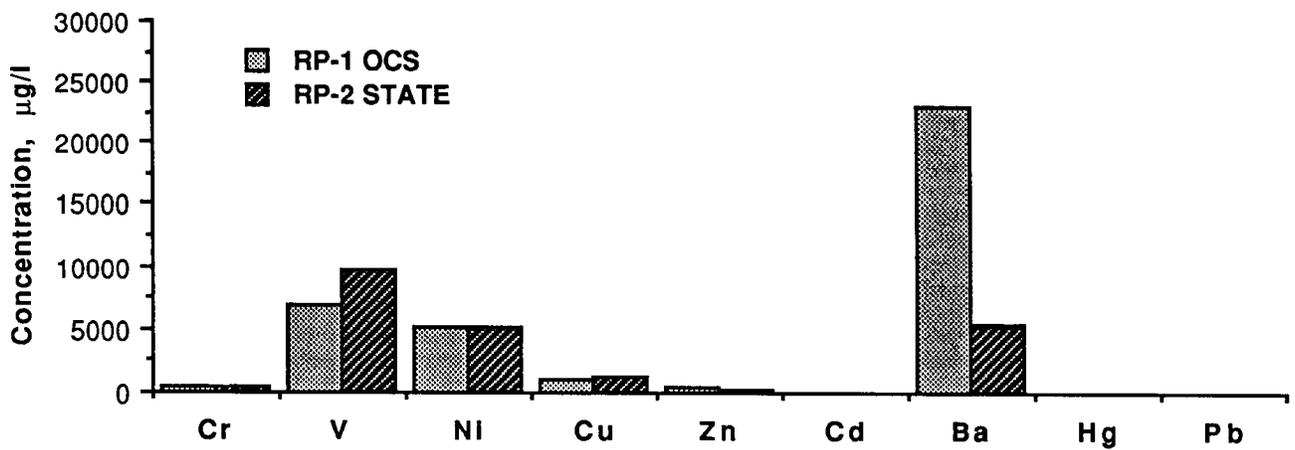
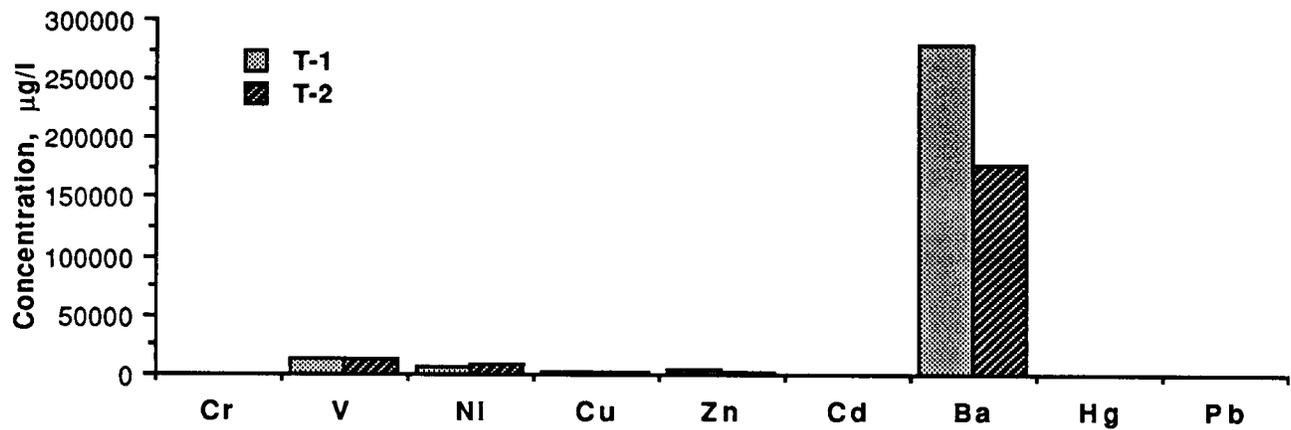


Figure 4.19. Concentrations of selected trace metals detected in produced water discharges from East Timbalier Island, Romere Pass and Empire Waterway.

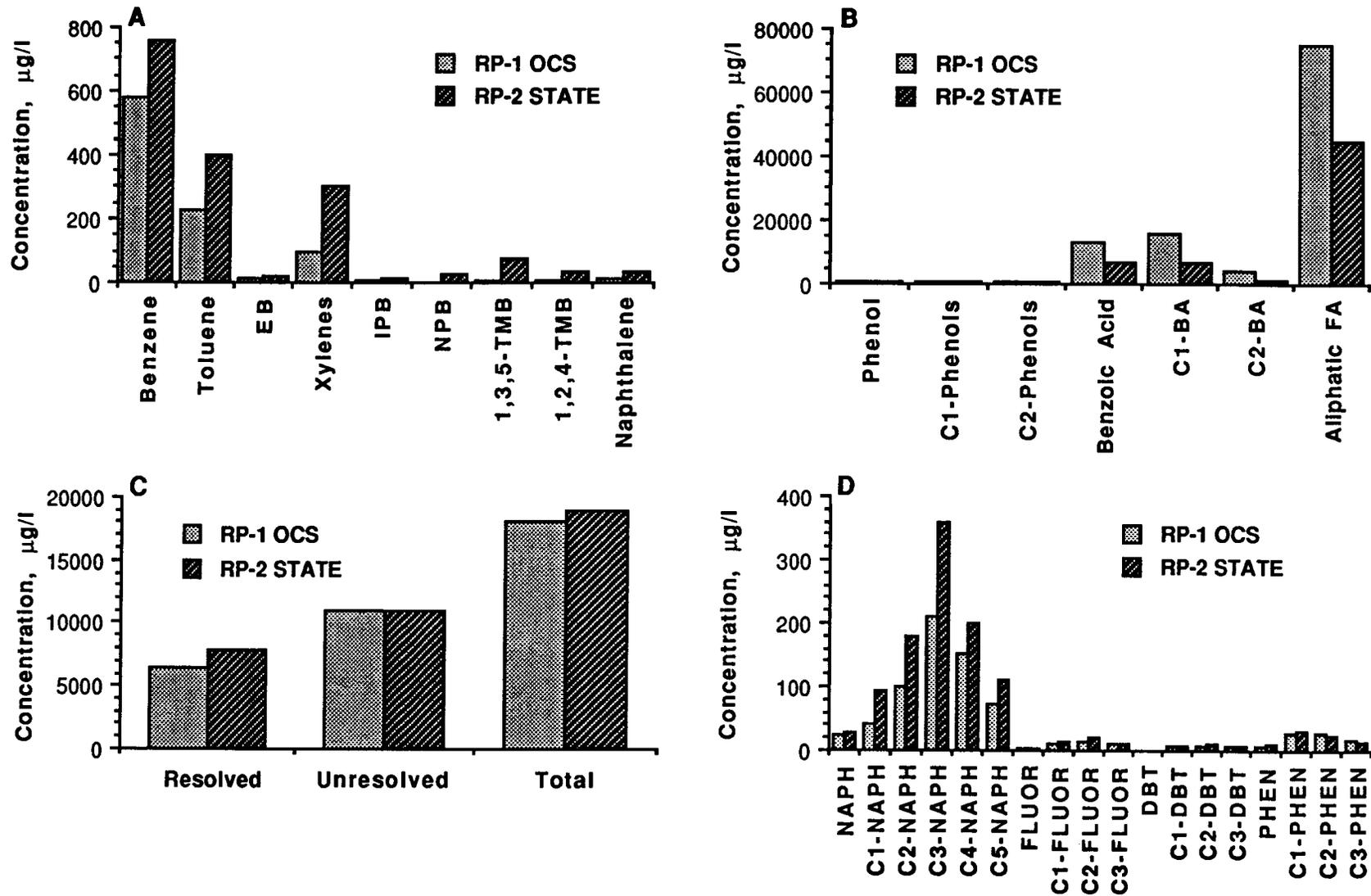


Figure 4.20 Concentrations of A) volatile hydrocarbons, B) acid-extractable compounds, C) saturated hydrocarbons and D) polynuclear aromatic hydrocarbons in Romere Pass produced water discharges RP-1 OCS and RP-2 State. (EB=Ethylbenzene, IPB=Isopropylbenzene, NPB=n-Propylbenzene, TMB=Trimethylbenzene, BA=Benzoic Acid, FA=Fatty Acid, NAPH=Naphthalene, FLUOR=Fluoranthene, DBT=Dibenzothiophene, PHEN=Phenanthrene.)

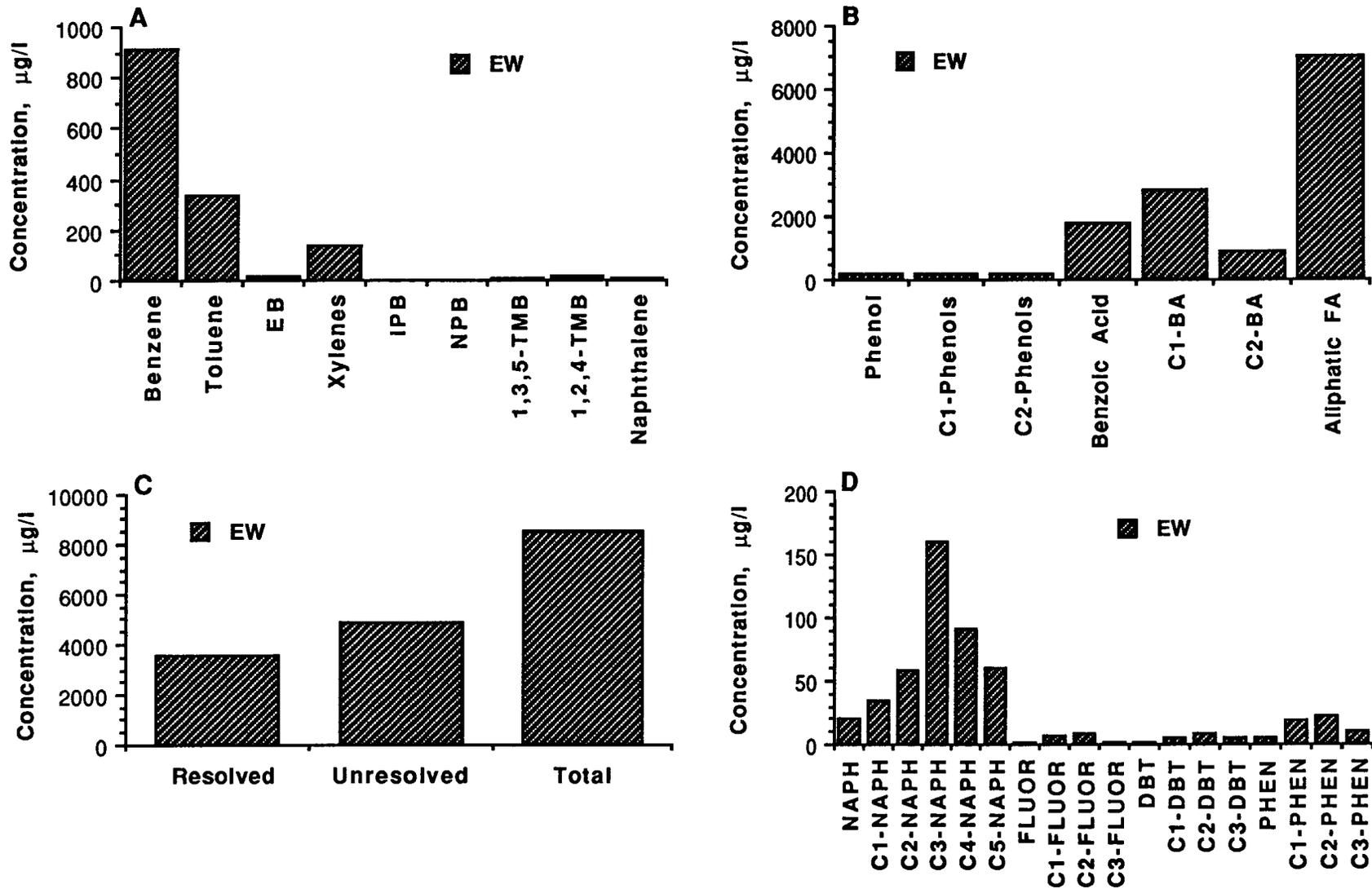


Figure 4.21 Concentrations of A) volatile hydrocarbons, B) acid-extractable compounds, C) saturated hydrocarbons and D) polynuclear aromatic hydrocarbons in the produced water discharge from Empire Waterway. (EB=Ethylbenzene, IPB=Isopropylbenzene, NPB=n-Propylbenzene, TMB=Trimethylbenzene, BA=Benzoic Acid, FA=Fatty Acid, NAPH=Naphthalene, FLUOR=Fluoranthene, DBT=Dibenzothiophene, PHEN=Phenanthrene.)

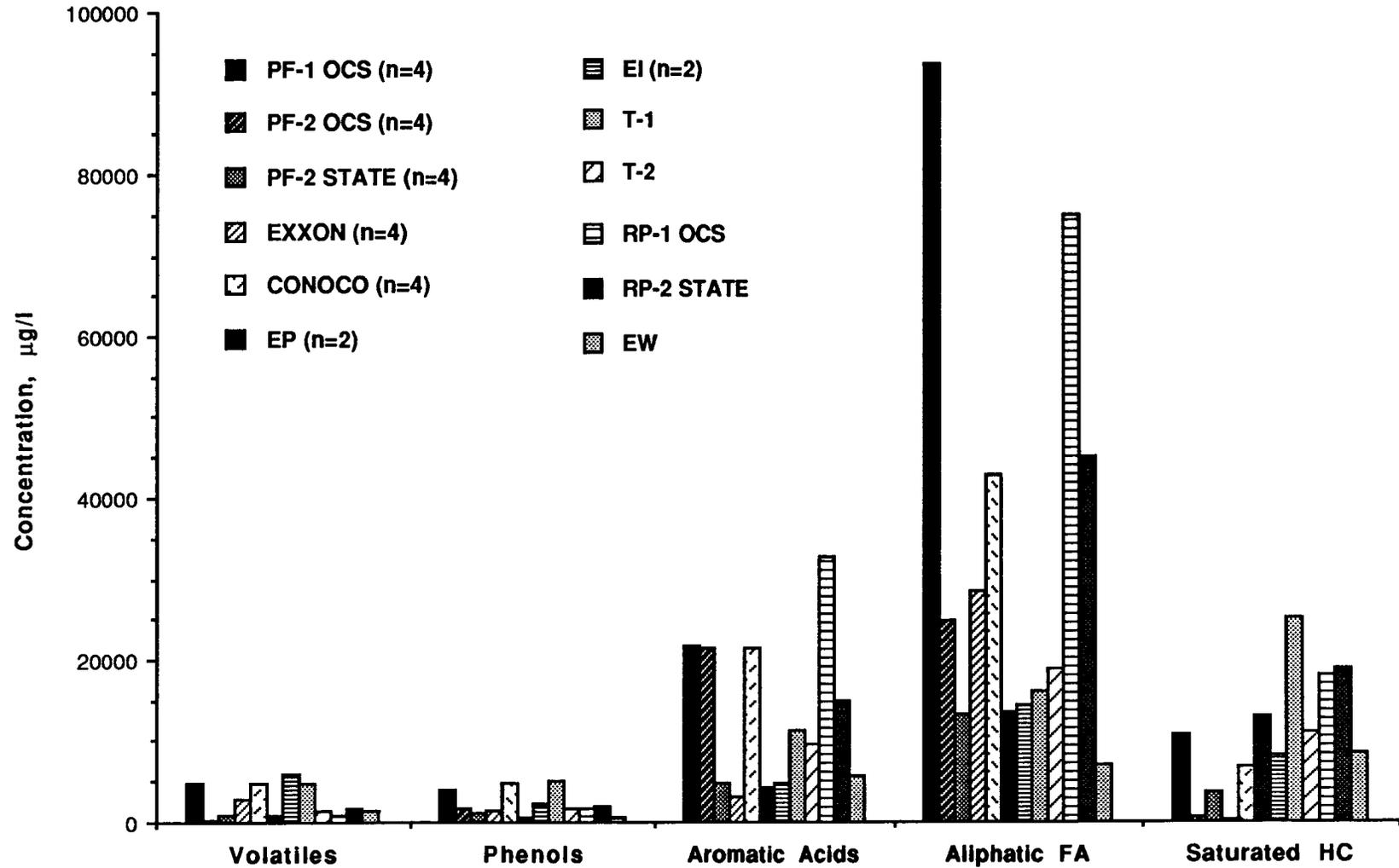


Figure 4.22. Comparison of volatiles, phenols, aromatic acids, aliphatic fatty acids and saturated hydrocarbons in 12 produced water discharges from this study. (n = number of discharge samples; FA=Fatty Acid, HC=hydrocarbon.)

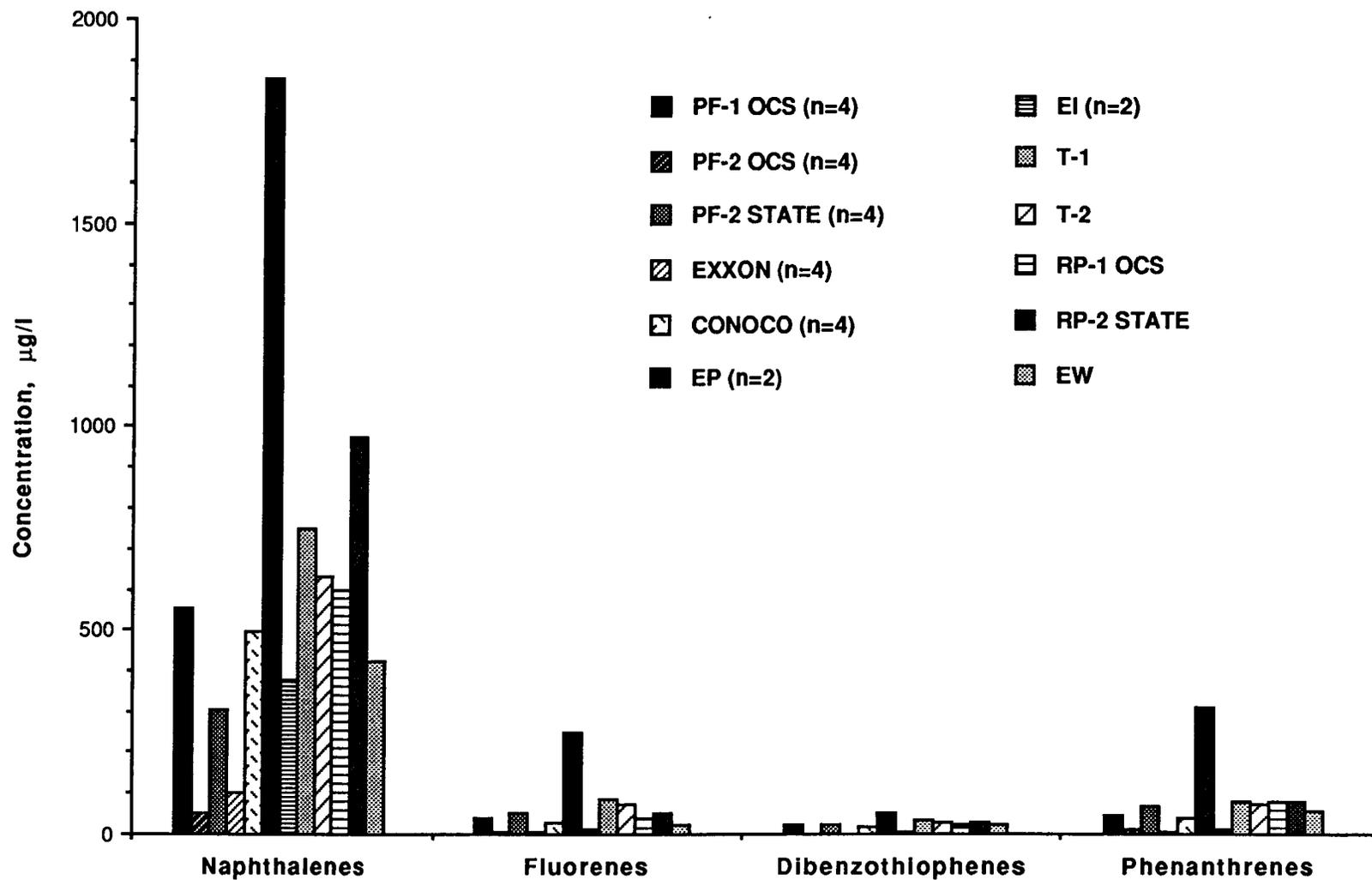


Figure 4.23. Comparison of polynuclear aromatic hydrocarbons in 12 produced water discharges from this study. (n = number of discharge samples.)

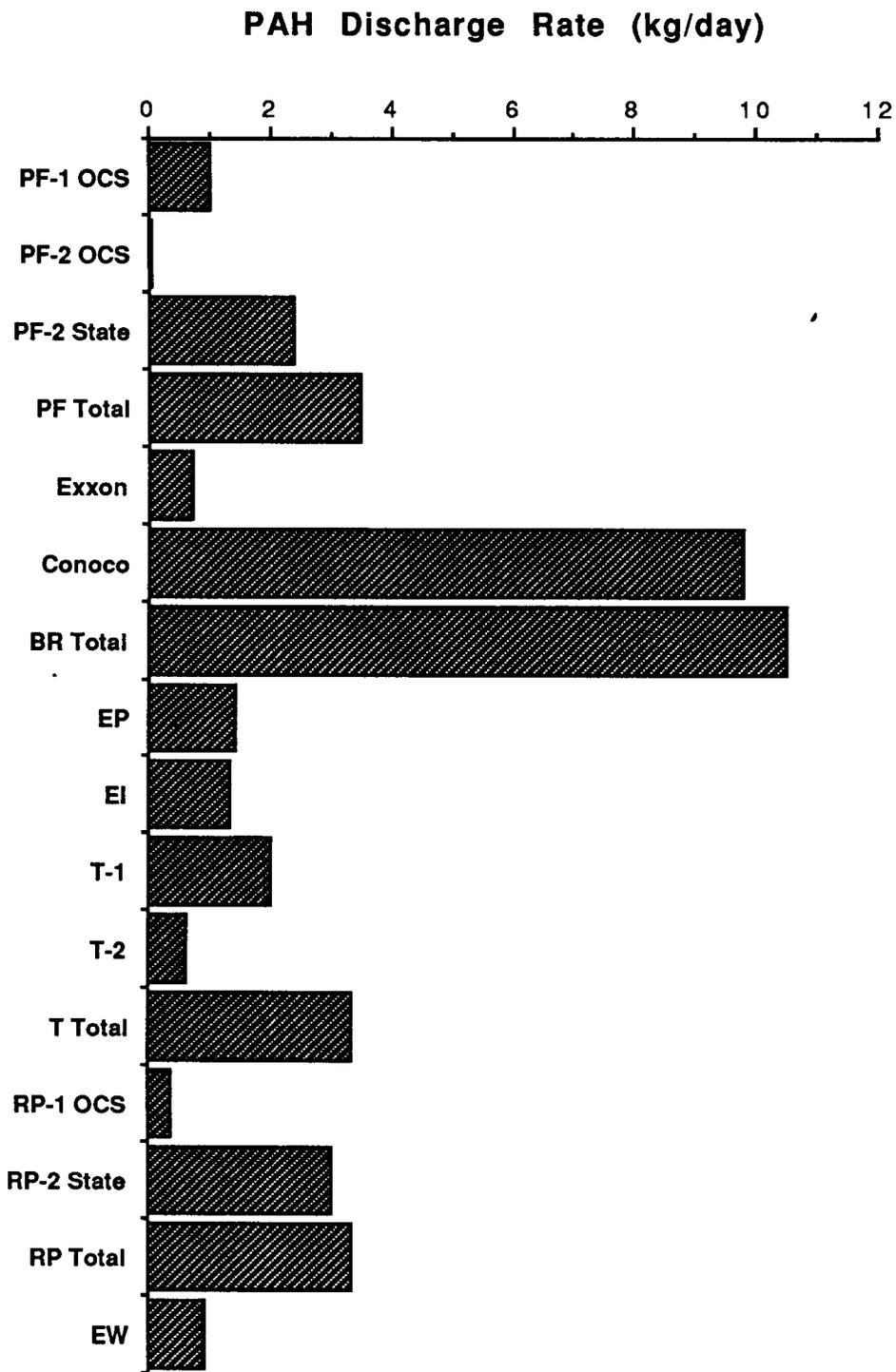
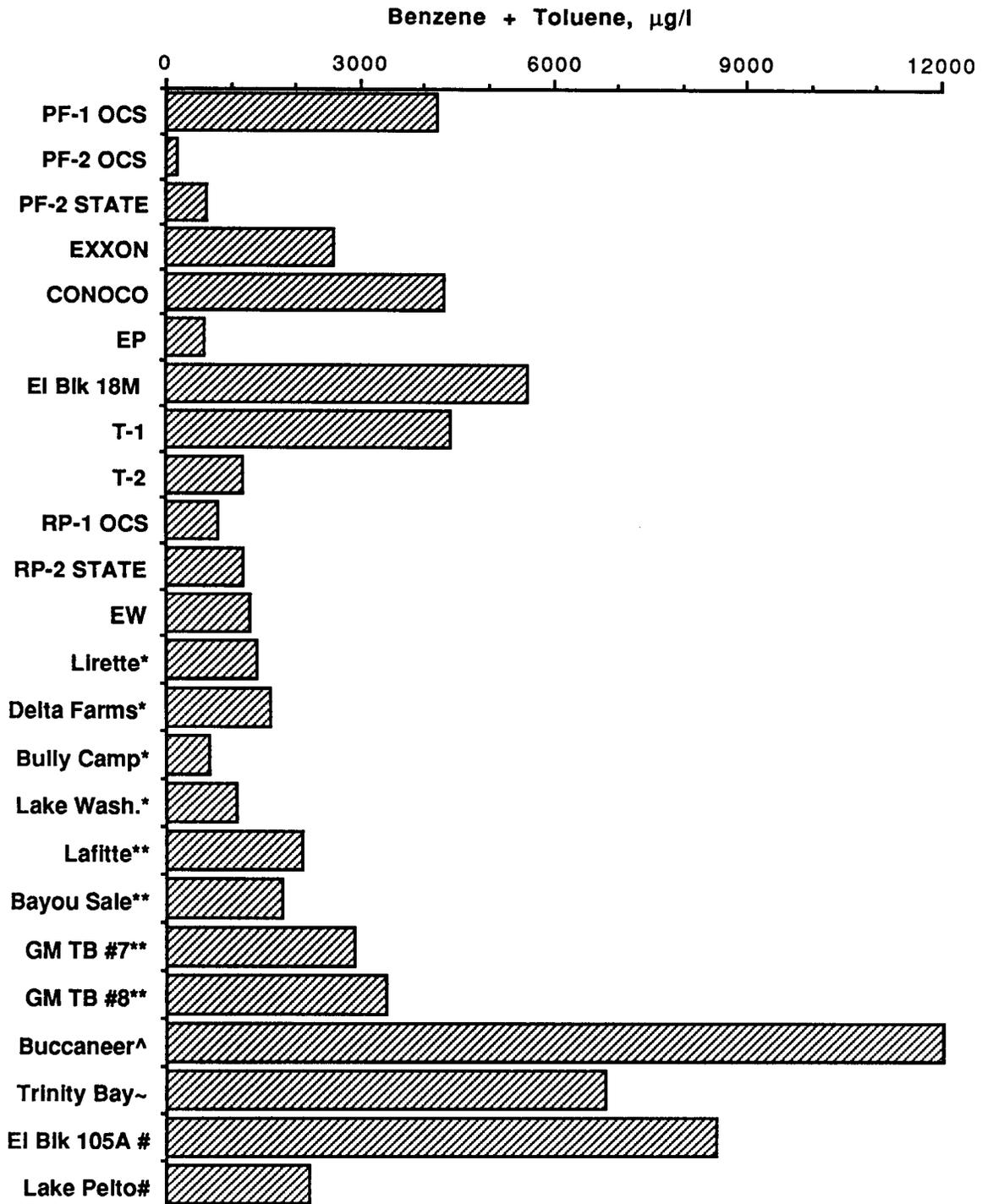


Figure 4.24. Comparison of PAH daily discharge rates for 12 produced water discharges in this study and the cumulative totals for Pass Fourchon (PF Total), Bayou Rigaud (BR Total), East Timbalier Island (T Total) and Romere Pass (RP Total).



* St. Pe' 1990

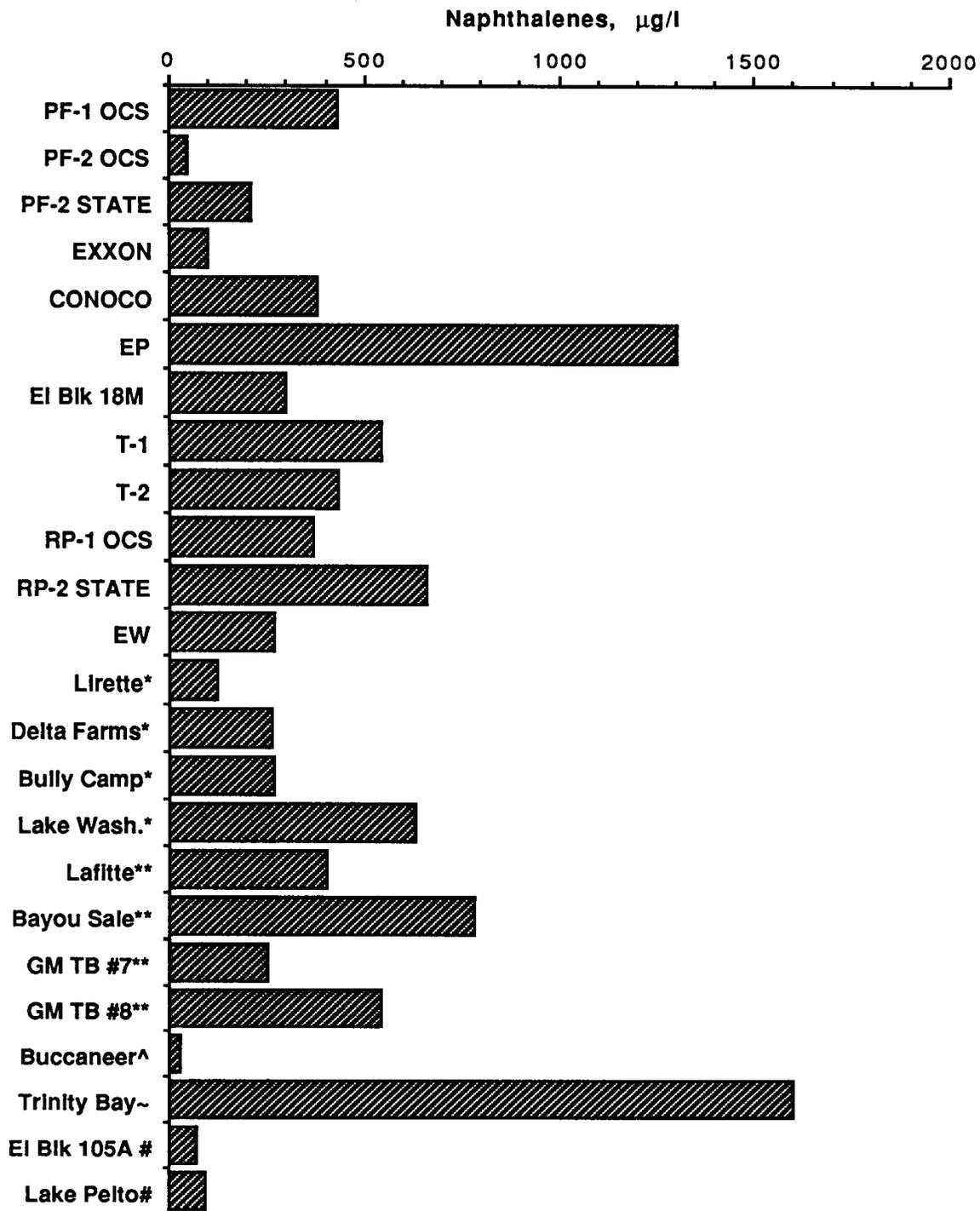
^ Middleditch 1981

Neff et al. 1989

** Boesch and Rabalais 1989 b

~ Armstrong et al. 1979

Figure 4.25. Comparison of benzene + toluene concentrations in 24 produced water discharges. (The first 12 discharges are those of this study; others as indicated.)



* St. Pe' 1990
 ^ Middleditch 1981
 # Neff et al. 1989

** Boesch and Rabalais 1989b
 ~ Armstrong et al. 1979

Figure 4.26. Comparison of the concentration of naphthalenes (C₀-C₃) in 24 produced water discharges. (The first 12 discharges are those of this study; others as indicated.)

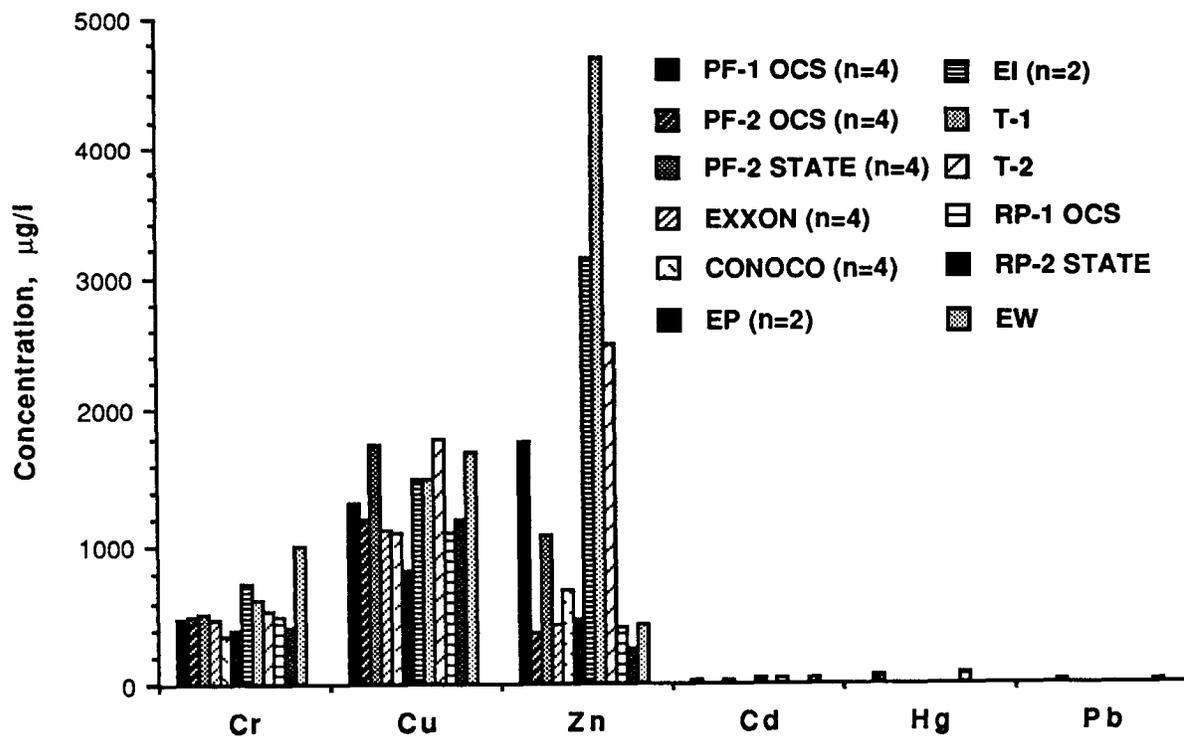
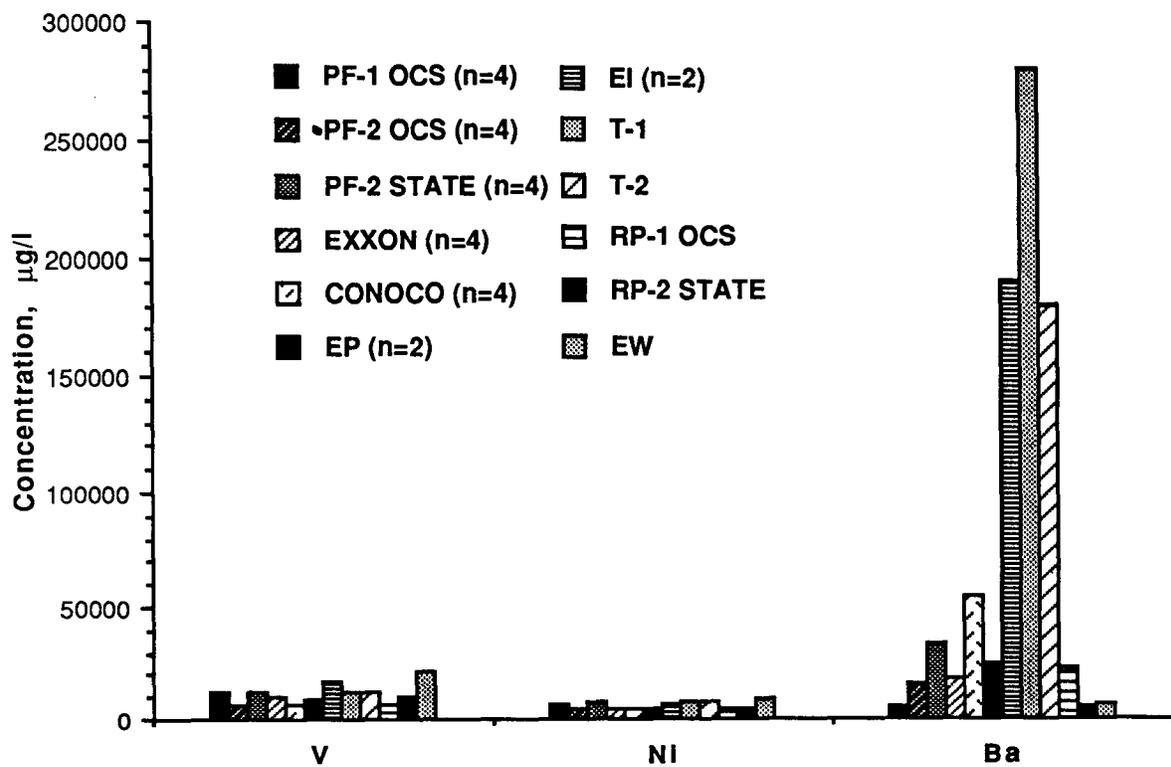
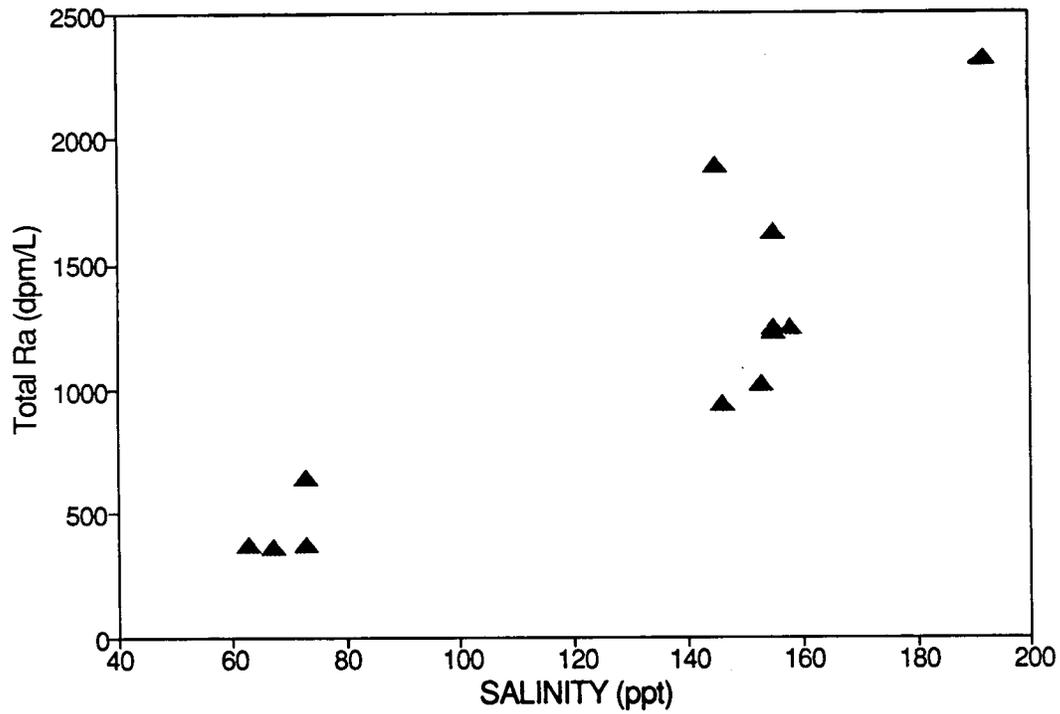


Figure 4.27. Comparison of the concentration of selected trace metals detected in 12 produced water discharges from this study. (n = number of discharge samples.)

PASS FOURCHON: DISCHARGE SITES



BAYOU RIGAUD: DISCHARGE SITES

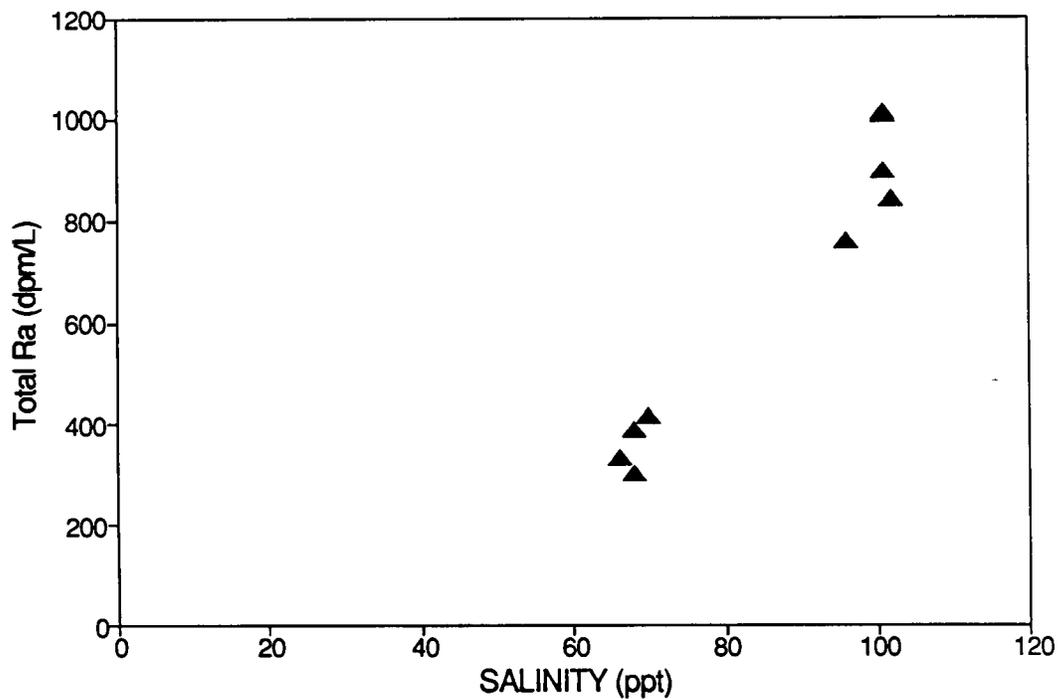


Figure 4.28. Relationship between total radium activity and salinity of produced water discharges at Pass Fourchon and Bayou Rigaud.

Chapter 5

PASS FOURCHON STUDY AREA

5.1. Description of Study Area

5.1.1 General Description

There are three discharges of produced waters at the Pass Fourchon study area. Two of these are generated on the Federally-controlled OCS and a third is generated within the State's territorial sea. All three discharges empty into a system of access canals near the terminus of the Pass Fourchon dead-end arm near the Gulf of Mexico shoreline (Figure 5.1). Two discharges enter a north-south access canal which joins an east-west access canal into which another discharge empties. The east-west access canal leads into Pass Fourchon near where the Pass itself is occluded by a sunken barge and a beach with shoreline stabilization structures. The dead-end arm of Pass Fourchon and the access canals are poorly flushed by tidal currents which are otherwise quite strong through Belle Pass and Pass Fourchon into Bayou Lafourche and the network of canals to the east of Pass Fourchon.

The ambient salinity of the Pass Fourchon area is strongly related to that of nearby Gulf of Mexico waters which in turn are influenced by the discharge of the Mississippi River (Geyer 1950). Salinities at the stations sampled during the study period ranged from 18 to 26 ppt, but mostly in the mid- to upper 20s. During a previous study (Boesch and Rabalais 1989a), salinities ranged between 27 and 28 ppt. Vegetation in the area was typical salt marsh vegetation, *Spartina alterniflora*.

Besides the produced water facilities, there is an oil storage tank facility (Sohio) located on the east-west access canal. The northern shoreline of Pass Fourchon is bulkheaded and lined with oil field service facilities, marinas and boat docks. The southern shoreline is salt marsh.

5.1.2 Facilities

PF-1 OCS is the Chevron U.S.A. Inc. Bay Marchand Barge discharge located on the northern shore of the east-west access canal (Figure 5.2). This facility was installed before 1960 (exact date unavailable) and has been in continual operation since then, excepting short periods of down-time for maintenance. The average discharge rate for the facility was $4,768 \text{ bbl} \cdot \text{d}^{-1}$ (mean of 25 monthly averages for February 1988 - February 1990) with a steady decline since February 1988 when the discharge was $7,000 \text{ bbl} \cdot \text{d}^{-1}$ (Table 5.1). The hydrocarbon levels of the discharge, reported as oil and grease content, averaged $19 \text{ mg} \cdot \text{l}^{-1}$ over the same 25-month period. The reported salinity of the discharge was 99.3 ppt chloride (179 ppt salinity). Representatives from Chevron indicated that there were no known treatment technologies which would significantly alter the chemical analyses. A fire occurred at the Pass Fourchon Bay Marchand Barge facility in early 1990 after the last collections for this study (February 1990). Although some produced water discharges were still ongoing in February 1990, work was proceeding to completely cease operations which occurred by March 1991. The production stream for PF-1 OCS has since been routed directly to the Fourchon Terminal (PF-2 OCS) for treatment and discharge.

PF-2 OCS is the Chevron Pipe Line Company Fourchon Terminal discharge located on the western shoreline of the north-south access canal (Figure 5.2). Chevron Pipe Line Company acquired the Fourchon Terminal from Chevron U.S.A. Inc. during the Chevron-Gulf merger. The facility was constructed primarily for the treatment of crude oil. To date, the facility has been in continual operation without any major interruptions since operations began in 1950. The

average discharge rate for the facility was $9,645 \text{ bbl}\cdot\text{d}^{-1}$ based on the four monthly averages reported in Table 5.1. Since the completion of our field studies in February 1990, this facility has been receiving more of the product stream from PF-1 OCS. The hydrocarbon levels of the discharge, reported as oil and grease content, averaged $40.1 \text{ mg}\cdot\text{l}^{-1}$ over the 25-month period of February 1988 - February 1990. The reported salinity of the discharge was 35,170 ppm chloride (63.5 ppt salinity). Representatives from Chevron indicated that there were no changes in the treatment process during the study period. No additives were used and the treatment consisted of heat and settlement only. This discharge had a notable black color that was attributed to the high sulfide content (see Table C.1 and Section 5.2.2); the sulfide is characteristic of the formation.

PF-2 State is the Chevron Pipe Line Company Fourchon Terminal discharge located on the eastern shoreline of the north-south access canal (Figure 5.2). This facility was acquired by Chevron Pipe Line Company as described above in the Chevron-Gulf merger. The facility has been in operation since 1950. The average discharge rate for the facility was $33,756 \text{ bbl}\cdot\text{d}^{-1}$ based on the four monthly averages reported in Table 5.1. The hydrocarbon levels of the discharge, reported as oil and grease content, averaged $27 \text{ mg}\cdot\text{l}^{-1}$ over the 25-month period of February 1988 - February 1990. The reported salinity of the discharge was 79,300 ppm chloride (143.2 ppt salinity). Representatives from Chevron indicated that there were no changes in the treatment process during the study period. No additives were used and the treatment consisted of heat and settlement only. A noticeable orange-brown color of the discharge was attributed to a high iron content.

The combined discharge rate of produced waters from the three facilities at the Pass Fourchon study area was approximately $48,000 \text{ bbl}\cdot\text{d}^{-1}$ as of February 1990 (Table 5.1). Previous estimates for this study area were $45,000 \text{ bbl}\cdot\text{d}^{-1}$ (Boesch and Rabalais 1989a). The February 1990 total estimate does not differ much from the previous one, however, the relative proportion of the three discharges is considerably different. The reported discharge rates were provided by the respective companies in written response (dated 09/90) to requests for information. The reduced discharge rate for the PF-1 OCS effluent is related to an overall reduction in the collection of water from the field (see above). This product stream has now been completely rerouted to PF-2 OCS. The current discharge rate for the PF-2 OCS effluent is now much higher than previous reports. Differences in the discharge rate for the PF-2 State discharge are likely related to the age of the field. The amount of water produced in the PF-2 State discharge has been steadily climbing as the petroleum reserves are depleted.

5.1.3 Study Design

A series of stations were located in the dead-end arm of Pass Fourchon where it terminates near the Gulf of Mexico shoreline (stations PF600S through PF800N) (Figure 5.2). Additional stations were located in Pass Fourchon proper (PF900N through PF1200N) and into the bayou which connects Pass Fourchon with Bayou Moreau (PF1000NE and PF1200NE). Six stations were sampled during each date for all water column and sediment characteristics, including vertical sediment cores, and are thus termed "secondary" stations in Figure 5.2. Only hydrographic profiles were taken at PF200, which was the docking facility for Chevron Pipe Line Company. No samples were taken at PF0 (the designated "zero" point, see below). Additional stations were sampled for water column and surficial sediment characteristics in May 1989. These stations are termed "primary" stations in Figure 5.2. The current meter station was a small boat anchor station between PF400 and PF500N. Samples were taken in February, May and October 1989 and February 1990.

Water depths in the dead-end arm of Pass Fourchon from PF600S to PF800N were 2.5 to 3.5 m. North of PF800N in Pass Fourchon proper, water depths reached 4 m. Several fathometer tracings were made along the dead-end arm of Pass Fourchon during the last cruise in February 1990 to determine where the deeper parts of the channel were located. Differences in

water column hydrography and in water column and sediment contaminants had been noted for previous sample dates depending on whether the ship had been anchored in such a way as to sample the deeper parts of the channel or not. The deeper parts of the channel were located mid-way or along the eastern shore. Bottom water and sediment collections at PF600N and PF800N were not always made at the deeper parts of the channel.

The data for the Pass Fourchon study site are plotted as a function of the distance away from the point of the produced water discharges. Due to the existence of multiple discharges at this site, an arbitrary "zero" point was selected approximately equidistant from all three discharges (PF0) and subsequent station names reflected a distance from this point (e.g., PF400 was approximately 400 m from this point, PF600S was approximately 600 m south of this point, PF800N was approximately 800 m north of this point). The data for the various parameters are plotted on a gradient of distance away from the discharge point with station PF400 being the focal point of the distributions.

5.2 Hydrography

5.2.1 Hydrographic Profiles

The effluent density plume for the multiple discharges into the Chevron access canal at the Pass Fourchon study area extended a minimum of 400 m to a maximum of 800 m from the designated "zero" discharge point (Figures 5.3 - 5.4; Tables A.1 - A.4). Between PF800N and PF900N, the waters of the dead-end arm of Pass Fourchon joined Pass Fourchon proper, and ambient conditions were reached at this juncture. Ambient conditions in Pass Fourchon were usually a well-mixed water column, but on occasion stratification was present. Receiving waters ranged from 14 to 28 ppt in salinity and from 15 to 27°C through the period of study.

In February 1989 the effluent density plume was restricted to the Chevron access channel and station PF400; otherwise the water column was slightly stratified. The average salinity of the multiple discharges was 147 ppt. A bottom water salinity of 43 ppt at PF200 indicated a 6-fold dilution of the density plume at that point. Ambient salinity in the dead-end arm of Pass Fourchon was 25 to 26 ppt. Bottom water salinity at PF400 was 31 ppt. For the remaining stations in the dead-end channel and into Pass Fourchon, the water column differed in surface-to-bottom salinity by 1 to 3 ppt. Water temperatures in February 1989 were 18 to 20°C with little thermal stratification. The water column was well-oxygenated at most stations (Table 5.2); exceptions were PF200 and PF400 where dissolved oxygen concentrations in bottom waters were between 1 and 2 mg·l⁻¹.

In May 1989 the effluent density plume extended as far as 800 m from the "zero" point, as well as into the occluded arm of Pass Fourchon (PF600S). The water column was well-mixed at stations 900 m or greater from the discharge point, both into Pass Fourchon proper and into the access canal to Bayou Moreau where additional stations were located for this sample period. The average salinity for the combined effluents was 136 ppt. A bottom water salinity of approximately 44 ppt at PF200 indicated a 3-fold dilution in salinity of the density plume at that station. Ambient salinity in the dead-end arm of Pass Fourchon was 21 ppt. Bottom water salinities at PF600N and PF800N were 40 and 36 ppt, respectively; these two stations were the deepest, and the density plume likely flowed along the lowest points in the bottom topography. Water salinity at 2.3 m depth at PF500N was 25.5 ppt, considerably less than the two adjacent stations (cf. 36 ppt and 40 ppt). It is likely, because of currents, that the bottom water was not sampled by the CTD unit at station PF500N; alternatively, this station was located at a topographically high area in the channel. Benthic community composition at PF500N, however, does not support the latter explanation (see Section 5.6). Although strong surface-to-bottom salinity differences (6 ppt) reached into the southerly occluded arm of Pass Fourchon (PF500S), these differences were not evident within 100 m at PF600S. Water temperatures in May 1989

were 25 to 27°C. At all stations where there was a surface-to-bottom salinity gradient (PF600S through PF800N), there were surface-to-bottom oxygen gradients (Table A.2). Dissolved oxygen concentrations were hypoxic ($< 2 \text{ mg}\cdot\text{l}^{-1}$) at PF200, PF600N and PF800N (Table 5.2).

During October 1989, the effluent density plume again extended up to 800 m from the "zero" discharge point. This month, however, the greatest surface-to-bottom salinity differences were found at PF800N instead of PF600N. The water column depth at PF800N was also greater than PF600N (3.1 m cf. 1.5 m). It is likely that the density plume flowed along the lowest points in the bottom topography and that the research vessel was anchored at PF600N in a different and shallower point than the previous month. The average salinity of the combined effluents was 133 ppt. A bottom water salinity of 43 ppt at PF200 indicated a 5-fold dilution of the salinity plume at that point. Ambient salinities were 26 to 27 ppt, and the water column was well-mixed at the most southerly and shallowest station (PF600S) and in Pass Fourchon (PF900N and PF1000N). Water temperatures in October 1989 were 24 to 26°C. At all stations where there was a surface-to-bottom salinity gradient, there were surface-to-bottom oxygen gradients (Table A.3). Dissolved oxygen concentrations were hypoxic ($< 2 \text{ mg}\cdot\text{l}^{-1}$) at PF200, PF600N and PF800N (Table 5.2). Ambient dissolved oxygen concentrations in surface waters and well-mixed water columns were low (3.2 to 4.3 $\text{mg}\cdot\text{l}^{-1}$). There were measurable concentrations of hydrogen sulfide in the near-bottom waters at station PF800N (8.4 $\mu\text{g-at S}\cdot\text{l}^{-1}$) (Table 5.2). Sulfide was trace in near-bottom water samples at the other stations.

The effluent density plume was limited to within 600 m of the "zero" discharge point in February 1990. The water column was stratified in Pass Fourchon proper with surface-to-bottom salinity differences of 9 ppt (PF1000N). The average salinity for the combined effluents was 127 ppt. A bottom water salinity of 40.6 ppt at PF200 indicated a 4-fold dilution in salinity of the density plume at that station. Bottom water salinities were highest at PF200 (40.6 ppt) and PF400 (33.8 ppt). While the CTD cast for bottom water salinity at PF600N did not indicate the presence of the effluent density plume, the collection of bottom water did (see below). The location of the deepest collection point in the dead-end arm of Pass Fourchon reversed in February 1990 from that of the previous sampling period, with PF600N being deeper than PF800N. Water temperatures in February 1990 were 14 to 17°C, 3°C cooler than the previous sample in February 1989. There were surface-to-bottom oxygen gradients at stations PF200, PF400 and PF600N. Dissolved oxygen concentrations were hypoxic ($< 2 \text{ mg}\cdot\text{l}^{-1}$) at PF200 and PF600N and approached anoxia at PF400 (Table 5.2). The hydrogen sulfide concentrations in the near-bottom water at PF600N were extremely high (130 $\mu\text{g-at S}\cdot\text{l}^{-1}$). Sulfide levels in near-bottom waters were trace or not detected for the remaining stations.

5.2.2 Dispersion of Effluent

The salinity of the combined produced water discharges at the Pass Fourchon facilities averaged 136 ppt over the study period. Evidence of the bottom-hugging density plume could be detected as far as 800 m to the north from the designated "zero" discharge point. On the one sample date when a station was located between PF400 and the end of the occluded channel, there was evidence that the density plume extended in the southerly direction. Otherwise the water column at PF600S was shallow and well-mixed. Stations PF200, PF400, PF600N and PF800N were those consistently influenced by the effluent density plume.

The interstitial salinity of surficial sediments collected from box cores were elevated above the ambient level during the period of study at PF400, PF500N, PF600N, PF800N, PF900N and PF1000N (Figure 5.5). Higher than ambient interstitial sediment salinities at PF900N and PF1000N were not likely due to the influence of the brine effluent, since they were within the range of salinities expected within Pass Fourchon and did not exceed 35 ppt salinity as did the others.

The hydrogen sulfide content of one of the discharges at Pass Fourchon was high ($113 \mu\text{g-at S}\cdot\text{l}^{-1}$). Elevated levels of sulfide at PF600N and PF800N could be related to the sulfide content of the brine effluent. In both cases, however, dissolved oxygen concentrations in near-bottom waters were below $0.5 \text{ mg}\cdot\text{l}^{-1}$ when sulfide concentrations were elevated. Anoxia, or conditions near anoxia, would favor the release of hydrogen sulfide from the sediments and/or a retention of these sulfides in the water column above the seabed. On the other hand, elevated sulfides in waters overlying the sediments would also strip oxygen from the water column.

The density plume followed the bottom contour at its greatest depths along the dead-end channel of Pass Fourchon. Depending on the anchoring of the research vessel, the CTD cast and bottom water collection were not always at the deepest point in the channel. During some months the water column sampled was shallower than in other months. Comparisons of these stations among sample periods, therefore, may be difficult if the deeper areas influenced by the density plume were not always sampled.

5.2.3 Tidal Current Regime

Tidal currents were measured at the Pass Fourchon study area for 25-hr periods during each sample period. Data sets are complete with the exception of three sets of readings in February 1990 when heavy rain caused problems with the current meter's internal batteries. The same anchor station was occupied between PF400 and PF500N in 2.5 to 3 m of water during each sample period with the current meter operated from a small boat. Tidal currents at this study area were negligible with velocities rarely exceeding $0.1 \text{ m}\cdot\text{s}^{-1}$ at any elevation in the water column or at any stage of the tide. There was insufficient tidal flow to orient the current meter and directional information was poor. For example, during sampling in February 1989 over 61% of the 247 velocity measurements taken were $0.03 \text{ m}\cdot\text{s}^{-1}$ or less, where $0.03 \text{ m}\cdot\text{s}^{-1}$ is the lower limit of the current meter's resolution. Given that such a high percentage of the readings were so low that the current meter could not be relied upon for accuracy, it was not possible to construct a detailed description of the tidal current regime for the Pass Fourchon study site. Similarly, the orientation of the current meter varied through the water column as there was insufficient current to maintain its position with regard to the flow. The situation was similar in subsequent sampling periods with 54.6% of readings being below $0.03 \text{ m}\cdot\text{s}^{-1}$ in May 1989, 68.8% in October and 44% in February 1990. Directional data gave some indication of tidal flow both into and out of the canal but was inconclusive regarding the duration of either flood or ebb tides, or their relative magnitudes. The current regime for the Port Fourchon study site can be characterized as low mean velocities, usually less than $0.05 \text{ m}\cdot\text{s}^{-1}$, on both flood and ebb tides.

5.2.4 Velocity Profiles

Because of the difficulty of accurately measuring small current speeds and the variation in directional readings for each current profile, it was not possible to determine shear velocities for most of the sample periods at Pass Fourchon. However, flow was occasionally sufficient and current direction consistent enough through the profile to calculate a shear velocity from the current meter data. For example, Figure 5.6 shows a velocity profile for 0900 on 9 May 1989 in 2.1 m of water. Current velocity was low, reaching only $0.06 \text{ m}\cdot\text{s}^{-1}$ at the surface. The shear velocity calculated from this profile, $0.88 \text{ cm}\cdot\text{s}^{-1}$, was low and probably insufficient to cause resuspension of bed material at this location. Overall, the velocity profile data at Pass Fourchon was not sufficiently reliable to calculate shear velocities. However, as current velocities were so low, it seemed unlikely that significant sediment entrainment and transport was occurring during the tidal cycles monitored.

5.3 Water Column Contaminants

5.3.1 Hydrocarbons

Figure 5.7 and Tables D.1 - D.4 show the volatile hydrocarbon and PAH data for near-bottom waters taken during four sample periods. Maximum volatiles were measured at PF600N during February 1990 ($94 \mu\text{g}\cdot\text{l}^{-1}$). The only stations where high volatiles were consistently detected were PF400, PF600N and PF800N. Volatiles were detected out to PF1000N during the February 1989 and October 1989 samples. The maximum PAH concentration found was also at PF600N during February 1990 ($24 \mu\text{g}\cdot\text{l}^{-1}$). Near-bottom waters from stations PF400 and PF600N contained detectable PAH in three out of the four sample periods. The volatile and PAH data follow similar patterns, indicating that these compounds have a similar source. There was no real trend in these data, possibly the result of: 1) the inability to sample consistently close enough the bottom to get a representative sample, 2) incomplete mixing of the discharge water with overlying water, because of slow water movement, or 3) the position where the sample was taken may be important, as the concentration of these compounds may not be homogeneous across the canal. It is interesting to observe that station PF400, which was closest to the discharge, was the highest station in volatiles and PAH only during the February 1989 sampling. This suggests that the produced water plume was probably not well mixed with the surrounding water and still very close to the bottom.

5.3.2 Radionuclides

Pb-210: During February 1989, Pb-210 activities in near-bottom waters generally decreased away from station PF400 (Figure 5.8, Table F.1). To the south, Pb-210 activities decreased from $3.11 \text{ dpm}\cdot\text{l}^{-1}$ at PF400 to $0.56 \text{ dpm}\cdot\text{l}^{-1}$ at PF600S. To the north, Pb-210 activities in near-bottom waters decreased from $3.11 \text{ dpm}\cdot\text{l}^{-1}$ at PF400 to $0.54 \text{ dpm}\cdot\text{l}^{-1}$ at PF1000N. This was a six-fold decrease in Pb-210 activities from the canal containing the discharges to the northernmost extent of the study area. However, near-bottom water Pb-210 concentrations were 31 times natural levels at PF400 and 5 times natural levels 1000 meters from the discharges.

During May 1989, Pb-210 activities in near-bottom waters ranged from 0.12 to $0.68 \text{ dpm}\cdot\text{l}^{-1}$ (Figure 5.8, Table F.1). No spatial trend was apparent. These Pb-210 activities were lower than observed in February 1989, perhaps reflecting the lower Pb-210 activities of produced waters during this time period. The May 1989 Pb-210 activities ranged from natural levels to activities that were 7 times natural waters.

During October 1989, Pb-210 activities in near-bottom waters ranged from 0.03 to $0.55 \text{ dpm}\cdot\text{l}^{-1}$ and exhibited no apparent spatial trend (Figure 5.8, Table F.1). Pb-210 activities were highest at PF600S where they were about 5 times higher than natural levels. Most of the samples collected had natural levels of Pb-210.

During February 1990, Pb-210 activities in near-bottom waters ranged from 0.05 to $0.34 \text{ dpm}\cdot\text{l}^{-1}$ (Figure 5.8, Table F.1). All stations, except PF400 had Pb-210 activities that were within the range of natural levels. At PF400 Pb-210 activities were about 3 times higher than natural waters.

Radium: In all water samples, U-238 and Th-234 activities were below detection levels (<0.5 and $<0.8 \text{ dpm}\cdot\text{l}^{-1}$, respectively). This lack of enhanced uranium and thorium activity indicates strongly that the high radioactivity levels associated with produced waters originate with the radium isotopes and is not supported by radioactive parents of radium which are higher in the decay chain. Total radium is the sum of Ra-226 and Ra-228 activities. The ratio of Ra-226/total Ra varies from site to site for produced waters, but in most cases the Ra-226 activity constitutes more than two-thirds of the total radium activity.

During February 1989, total radium activities in near-bottom waters generally decreased away from station PF400 (Figure 5.9, Table F.1). To the south, total radium activities decreased from $106 \text{ dpm}\cdot\text{l}^{-1}$ at PF400 to $81 \text{ dpm}\cdot\text{l}^{-1}$ at PF600S. To the north, activities decreased from $106 \text{ dpm}\cdot\text{l}^{-1}$ at PF400 to $84 \text{ dpm}\cdot\text{l}^{-1}$ at PF1000N. Total radium activities at intermediate stations varied from 69 to $87 \text{ dpm}\cdot\text{l}^{-1}$. Near-bottom water total radium concentrations were 53 times natural levels at PF400 and were still 42 times natural levels 1000 meters from the discharges.

During May 1989, total radium activities in near-bottom waters ranged from 43 to $173 \text{ dpm}\cdot\text{l}^{-1}$ (Figure 5.9, Table F.1). No general spatial trend was apparent; however, activities paralleled salinities closely. The May 1989 total radium activities ranged from activities that were 21 to 87 times natural waters.

During October 1989, total radium activities in near-bottom waters ranged from 65 to $141 \text{ dpm}\cdot\text{l}^{-1}$ and exhibited no apparent spatial trend but correlated with salinity (Figure 5.9, Table F.1). Activities were highest at PF800N where they were about 70 times higher than natural levels. Most of the samples collected had activities greater than 40 times natural levels.

During February 1990, total radium activities in near-bottom waters ranged from 51 to $127 \text{ dpm}\cdot\text{l}^{-1}$ (Figure 5.11, Table F.1). Activities decreased by a factor of 2 between PF400 and PF1000N. Total radium activities were more than 25 times natural levels at 1000 meters from the discharges.

5.4 Sedimentary Characteristics

5.4.1 Grain Size Distribution

During early 1989 (February and May), grain size distributions of surface sediments at all Pass Fourchon stations could be characterized as muddy sand. Samples were typically greater than 70% sand and less than 5% clay (Figure 5.10, Table B.1). Sand content increased north of PF800N in both February and May 1989, with the exception of PF1200N. This spatial trend continued in samples from October 1989 and February 1990, and as the sand content of all samples decreased, the grain size distribution could be characterized as a combination of muddy sands and sandy muds. Stations PF400, PF600N and PF800N all showed marked increases in silt content between May and October 1989 to >60%, >50% and >50% respectively (Figure 5.11). PF600S, PF900N and PF1000N continued to show increased sand content over other stations. This was probably caused by either proximity to the back of the sandy barrier shoreline and recent dredge spoil (PF600S) or the higher energy nature of the main Belle Pass - Bayou Moreau channel.

5.4.2 Sediment Total Organic Carbon (TOC)

Results from TOC analyses showed variation between stations in February 1989. For all stations except PF900N and PF1000N, values were between 1.2 and 1.7% (Figure 5.12, Table B.1). The two northernmost stations, which are in the main Belle Pass - Bayou Moreau channel, had TOC contents of less than 0.2%. This decrease was broadly associated with an increase in sand content at these stations. The pattern was similar in May 1989 when more stations were sampled. Again highest values (between 1 and 2%) were found in the main north-south channel with decreased values north of PF800N. This grouping was also broadly correlated with grain size data with highest TOC values found in areas with highest silt and clay content. The main changes found in October 1989 and February 1990 were in magnitude rather than distribution. For example, TOC at PF900N increased to 1.1% in October but was 0% in February 1990. The figures also show variations in TOC at PF400 and PF600N, increasing to approximately 2% in February 1990.

5.5 Sediment Contaminants

5.5.1 Hydrocarbons

5.5.1.1 Surficial Sediments

The concentrations of normal petroleum hydrocarbons as well as petrogenic alkylated aromatic hydrocarbons (alkylated PAH), related pyrogenic aromatic hydrocarbons (parent PAH), and Fossil Fuel Pollution Index (FFPI) are shown in Figures 5.13 - 5.16 and detailed in Tables D.16 - D.19.

In February 1989, alkylated PAH concentrations were observed to be maximal at PF600N and decreased in both directions from this point. The alkylated PAH concentrations were reduced by several orders of magnitude at PF900N and PF1000N. This was probably due to a large difference in the tidal flushing at these two stations relative to that occurring at stations in the dead-end canal. The alkylated PAH were the dominant forms present in the sediments in this study region, with parent PAH contributing relatively little to the total PAH load except at PF900N where parent PAH were the dominant PAH species present. This was reflected in the FFPI value at PF900N which dropped to <0.1 while at all sites within the canal it was greater than 0.8. The decrease in concentrations observed at PF600S may be due to the decreased flow occurring in the direction of this dead-end canal.

Aliphatic hydrocarbon concentrations in the sediments followed the same patterns as the alkylated PAH concentrations. The dramatically reduced concentrations observed at the PF900N and PF1000N also support the hypothesis that transport and flushing may rapidly disperse hydrocarbons leaving the dead-end portions of the canal.

In May 1989, five additional stations were collected. In general, the same patterns of aromatic hydrocarbon concentrations were observed. Alkylated PAH dominated the distributions as reflected both in the spatial distribution plots of the two types of PAH as well as in the plot of FFPI. Again substantial decreases in alkylated PAH concentrations at PF900N and PF1000N were observed. Two additional stations, PF1000NE and PF1200NE also exhibited very low alkylated PAH concentrations and decreased FFPI values. In May 1989, the maximum alkylated PAH concentrations were observed at PF500N (~38,000 ppb) rather than PF600N as in February. This is likely due to the result of site-related variability. The lowered FFPI value observed at PF500S in May indicated that some significant amounts of pyrogenic PAH had been introduced into the region at this location. Note that at PF600S the FFPI was near 0.8 which was similar to the value in February.

Aliphatic hydrocarbon patterns in May surficial sediments followed the same patterns as the alkylated PAH. The maximum value observed (900,000 ppb) was higher than that measured in February. This may be due in part to accumulation over the intervening period of time or to spatial variation.

The results from October 1989 show some differences from the preceding two sample periods. First, alkylated PAH concentrations were lower at PF600N and PF800N. In February alkylated PAH concentrations as high as 28,000 ppb were observed at PF600N, while in October, the maximum observed was less than 2,000 ppb. A decrease of approximately half was observed for these compounds at PF800N in October. Alkylated PAH concentrations at PF400 and all of the other stations were similar in these two months. This suggests variability in the location of box core positioning and heterogeneity of the sediments and hydrocarbon distributions. Sediment transport at this location was an unlikely explanation based on the decrease in sand content and increase in silt content between May and October 1989 (Table B.1)

and on the low current velocities and lack of evidence for sediment entrainment (see Section 5.2.4).

Aliphatic hydrocarbon concentrations in surficial sediments in October showed a pattern very similar to the alkylated PAH. A large decrease in total HC was also observed at PF600N in October, even though in general total HC concentrations were higher at most other stations in the region as compared to either February or May 1989 samples.

In February 1990 the alkylated PAH concentrations were generally higher than at any previous sample time. The spatial distribution of the alkylated PAH were very similar to those observed in the preceding three dates. Maximal concentrations of alkylated PAH were observed at PF400 with decreases away from the station as has been observed previously. The spatial distribution of aliphatic hydrocarbons in the February 1990 samples was very similar to those of the alkylated PAH.

Figure 5.17 shows the temporal changes in the alkylated PAH concentrations at three stations over the course of the year. While alkylated PAH concentrations increased at PF400 with a large increase occurring between October 1989 and February 1990, a general decline was observed at PF800N. At PF600N a successive decline which was observed from February 1989 through October 1989 was reversed by a greater than 30-fold increase observed in February 1990. Temporal changes in total HC concentrations showed a dramatic increase between October 1989 and February 1990 in the concentrations of these substances in sediments at PF400 and PF600N. A declining trend at PF600N was reversed in February 1990, while a steady increase was observed over the entire study period. Total hydrocarbon concentrations steadily declined at PF800N.

Overall, the spatial distributions of the alkylated hydrocarbons and total petroleum hydrocarbons show that the produced water discharges are having a substantial impact upon the sediments in the study site to a distance of one kilometer from the "zero" discharge point. This conclusion as well as the origins of the hydrocarbons are confirmed both by the FFPI values as well as comparisons of the relative abundances of the compounds found in the sediments with those discharged. Beyond this distance, the effects appear to be greatly reduced primarily due to increased water exchange beyond PF800N, which favors transport and diffusion of the hydrocarbons as well as a greater percentage of sand in the sediments beyond PF800N.

5.5.1.2 Vertical Profiles

Discussion of vertical sediment core sections taken at Pass Fourchon refers to Tables D.32 - D.43. Figures 5.18 and 5.19 show PAH and total HC/FFPI values for the collection in February 1989, respectively; and Figures 5.20 and 5.21 show the corresponding data for the February 1990 collection. Where possible, the concentration scale was kept constant for data from each station for a single collection to allow for visual comparison. Relative composition of alkylated PAH is discussed as percentages of total PAH. In general, fluorenes and dibenzothiophenes (DBT) averaged 10% or less and are not discussed further unless variations were noted. Naphthalenes and phenanthrenes tended to have an inverse relationship related to weathering effects and are discussed to provide an additional measure for comparison with the ratio of resolved/total (R/T) HC.

5.5.1.2.1 February 1989 Collection

PF400: Vertical core sections for PF400, closest to the discharge, had an average total PAH concentration of 20,000 ppb for all sections, and an average of 500,000 ppb total HC. A drop in these concentrations in the 15-20 cm section, followed by a rise at 20-25 cm, did not influence the FFPI, which remained constant at an average value of 0.92 for all sections. The

ratio of resolved/total HC averaged 0.06, indicative of a high degree of weathering of petrogenic contaminants. The average composition of petrogenic contaminants relative to total PAH in PF400 core sections was as follows, in order of greatest abundance: Naphthalenes, 64%, phenanthrenes, 16%, fluorenes, 9%, and DBT, 8%. For naphthalenes, the C3 through C5 homologs comprised greater than 90% of the total naphthalenes.

PF600N: This core showed highest concentrations of alkylated PAH, 28,000 ppb, and total HC, 580,000 ppb, at the surface, with a secondary peak in PAH from 15-25 cm and in total HC at 20-25 cm. Overall average concentrations were 23,000 ppb alkylated PAH and 460,000 ppb total HC, similar to PF400. The FFPI was again constant, averaging 0.93 for all depths, while the ratio R/T averaged 0.12, indicating a high degree of weathering of hydrocarbon contaminants, but slightly less than at PF400. The PAH composition was similar to PF400, with steady averages for naphthalenes and phenanthrenes of 68% and 15%, respectively, of total PAH concentration.

PF800N: The PF800N core showed a pattern of decreasing concentrations of petrogenic constituents with depth. The greatest concentration of alkylated PAH, 21,000 ppb, was found in the 2-5 cm section. The greatest concentration of total HC was in the surface section, 370,000 ppb. Overall, concentrations in this core were somewhat lower than PF400 and PF600N. The FFPI was fairly constant with depth, averaging 0.89. The ratio R/T was somewhat higher in the surface section, 0.18, but averaged 0.10 throughout the core, similar to PF600N. Composition of total PAH varied with depth in this core. Naphthalenes comprised 39% of the total PAH in the surface (0-2 cm) section, then rose to an average of 63% for sections 2-5 cm and 5-10 cm, and fell again to an average of 46%. An inverse pattern was evident for the phenanthrenes. Although not shown by FFPI values, the decrease in naphthalenes at lower depths may indicate a greater age of petrogenic contaminants, with reduction of naphthalene components through weathering effects.

PF900N: The PF900N core showed only trace levels of alkylated PAH and minimal parent PAH concentrations that were highest in the 15-20 cm section at 900 ppb. Hydrocarbon concentrations were low and averaged 1200 ppb total HC down through the 10-15 cm section, then increased to an average of 7,700 ppb between 15 and 40 cm. Even these higher values were considerably lower than in the previous stations. FFPI values were low, indicating minimal petrogenic inputs. The ratio R/T was somewhat higher than at previous stations, most likely a reflection of the low levels of total HC, and plant inputs to resolved HC.

PF1000N: Sediment samples from this core showed low levels of PAH, and total HC levels slightly higher than in PF900N, with no clear pattern due to depth. The FFPI was 0.52 at the surface, dropping to a low of 0.04 at 25-30 cm. This low value was the result of high parent (pyrogenic-source) PAH concentration, 1,300 ppb total, the highest value in Pass Fourchon samples from February 1989. The surface section was the only section to show a complete array of the targeted PAH, and was composed of 29% phenanthrenes, 13% naphthalenes, 8% fluorenes, and 4% DBT, expressed as a percentage of total PAH. The relative disappearance of naphthalenes compared to other stations indicated a high degree of weathering.

PF600S: Three maxima were apparent in both alkylated PAH and total HC concentrations for the vertical core from PF600S. Areas of highest values occurred at 5-10 cm, 20-30 cm, and 35-39 cm. Highest concentrations were 6,200 ppb alkylated PAH at 35-39 cm, and 270,000 ppb total HC at 5-10 cm. Overall averages of PAH and total HC were intermediate to those from other stations, and similar to values from the lowest depths of PF800N. The FFPI roughly followed the same pattern as alkylated PAH and total HC, but was generally lower than PF400, PF600N and PF800N. Average composition relative to total PAH was 55% naphthalenes and 21% phenanthrenes similar to PF800N.

5.5.1.2.2 February 1990

PF400: The vertical core sections from this station showed a pattern of generally decreasing concentration with depth for alkylated PAH and total HC. Highest concentrations, at the surface, were 89,000 ppb alkylated PAH and 1,700,000 ppb total HC. The FFPI values were fairly consistent between sections and averaged 0.90. The ratio R/T averaged 0.12, decreasing from 0.19 at the surface, to a low of 0.07 in the 30-35 cm section. The relative composition of total PAH was 64% naphthalenes and 14% phenanthrenes. Concentrations in this core were considerably higher at the surface than for the core taken in February 1989, but were similar near the bottom of the core, suggesting an increase in contaminant loading. The average R/T value was higher, indicating a lesser degree of weathering than for the 1989 sample.

PF600N: The "S"-shaped pattern for this core was similar to the core taken the previous year, with a maximum level of alkylated PAH and total HC at the surface, followed by a decrease, then a rise to slightly below surface levels at 20-25 cm, followed by a decrease toward the bottom of the core. Concentrations were 57,000 ppb alkylated PAH and 1,300,000 ppb total HC in the surface section. These values were a slight decrease from PF400, but again, as for PF400, the concentrations were considerably higher than for the same station sampled in 1989. FFPI values were constant throughout the core, averaging 0.93. Also similar to PF400, the R/T values were somewhat higher than in 1989. In contrast to the core from 1989, the composition of total PAH for the 1990 core appeared to decrease from an average of 72% naphthalenes at the surface through 20 cm, to an average of 52% for sections 20 cm through 39 cm. Phenanthrenes averaged 17% of total PAH throughout for all sections, and showed an inverse pattern, i.e., an increase in relative concentration below 20 cm. The ratio R/T also showed a slight decrease below 20 cm, and supported the conclusion that petrogenic contaminants in lower sections of this core were somewhat more weathered than those in the upper sections.

PF800N: The pattern for this core showed a general increase in both alkylated PAH and total HC with depth. This was the opposite of the trend noted in the 1989 core. Alkylated PAH showed the highest concentration, 3800 ppb, at 25-31 cm. Total HC averaged 68,000 ppb throughout the core; this was considerably lower than the previous stations, and was also lower than concentrations observed for the 1989 core. Extracted ion chromatograms for the top three sections showed an atypical hydrocarbon pattern, indicating a weathered, light fuel oil. Based on data from discharge samples and overlying water samples, this was probably an input from a source other than a produced water discharge. This alternate-source hydrocarbon pattern was also evident in cores taken at stations PF900N and PF1000N, and may be present in PF600N, its presence could be masked by the high levels of crude oil contamination. The FFPI values were generally around 0.90, but dropped to 0.37 in the 10-15 cm section, the result of high parent PAH contributions, especially the 4-ring PAH. R/T ratios were highest at 2-5 cm, 0.30, and fell to a low of 0.09 at 15-20 cm, indicating that HC nearer the surface were somewhat less weathered, similar to PF600N. The naphthalenes contribution to total PAH was lowest in the surface section and the 10-15 cm section, 30% and 29%, respectively, while other sections showed typical values, around 60%. The three sections showing light fuel oil contamination had higher naphthalenes percentages than the surrounding sections, leading to difficulty in identification of the source of these components.

PF900N: Generally low in hydrocarbon concentrations, PF900N showed a subsurface maximum in the 2-5 cm section, a result of the light fuel oil discussed above. The FFPI values followed the same trend; this index cannot be used to distinguish between different types of petroleum sources. R/T values ranged from 0.12 to 0.53, averaging 0.36, and were the highest, along with PF1000N (below), observed at all Pass Fourchon locations or vertical sampling times. Most PAH were at trace levels, and, where detected, were of typical composition. Total HC concentration apart from the light fuel oil contamination were similar to the 1989 core.

PF1000N: This core showed a subsurface maximum in alkylated PAH and FFPI similar to station PF900N, while the maximal total HC concentration occurred in the surface section, with a secondary maximum at 10-15 cm. The three sections with highest concentrations showed evidence of light fuel oil contamination similar to that noted in PF800N and PF900N. Apart from this alternate-source input, concentrations were low compared to other stations at Pass Fourchon. Total HC in sections not influenced by the light oil contamination were highest in the 15-19 cm section, at 22,000 ppb. Similar to PF900N, R/T values averaged a relatively high 0.37, except for the 5-10 cm segment, where the value fell, along with all other values, to 0.19. The composition of PAH was typical, with naphthalenes at 66% of total PAH. Alkylated PAH and total HC were detected at greater concentrations compared to the core taken in 1989.

PF600S: Three peaks in total HC concentrations were evident in this core, at 2-5 cm, 15-20 cm, and 30-36 cm. The greatest concentration, 120,000 ppb, was observed in the 15-20 cm section. Alkylated PAH was maximal in the 30-36 cm section, at 1,100 ppb. FFPI values tended to follow the total HC pattern, but were generally low, with a high value of 0.44 at 10-15 cm. These low values were due to low levels of alkylated PAH, which showed erratic composition and were generally found only at trace levels. The ratio R/T was generally low, 0.05, except for the 15-20 cm section, with a value of 0.49, indicative of a lesser degree of weathering. The overall pattern in this core was similar to the core taken in 1989, with an upward shift. This shift was probably the result of box core positioning or compaction of the sediment either before or after sampling. Concentrations of total HC were similar, while alkylated PAH tended to be lower than for the previous year.

5.5.1.2.3 Summary and Comparison between 1989 and 1990

Vertical core sections showed no consistent patterns with depth, between stations, or between years, indicative of random mixing of sediments by biota, vessel activity or dredging, spatial heterogeneity and/or sampling variability. In general total HC, alkylated PAH and FFPI values decreased with distance from the discharge, regardless of depth in the core. The patterns of alkylated PAH and total HC were usually similar for a particular core. The "S"-shaped pattern observed in concentrations at PF600N were similar for the two sample periods analyzed, with the exception that concentration in the 30-35 cm section in 1989 increased over shallower sections, while in 1990, these concentrations continued to decrease. Concentrations were relatively higher at PF400, PF600N, PF900N and PF1000N, and lower at PF800N and PF600S in 1990 compared to 1989. For 1990 cores, stations PF800N, PF900N and PF1000N showed evidence of contamination by a weathered, light fuel oil, which appeared in the top two to three sections and contributed to a majority of the total HC concentration.

5.5.2 Trace Metals

5.5.2.1 Surficial Sediments

Trace metal concentrations in surficial sediments from Pass Fourchon are detailed in Tables E.1 - E.4. Figure 5.22 shows the spatial distributions for each sample period for Ba, Zn and Ni, metals associated with produced water discharges (Neff et al. 1989), and which were the most abundant metals (excluding Al) in these sediment samples. Except for February 1989, concentrations of Ba were highest at PF400, closest to the discharges. PF600N showed the highest value of Ba from February 1989 and had the second highest values for the other periods. Ba concentrations for February 1990 were doubled compared to previous samples. Comparison with Figure 5.19, shows that Ba concentrations correlated well with spatial and temporal distributions of petroleum hydrocarbons. Zn and Ni concentrations were approximately one-tenth of the Ba concentrations. Spatial distributions of Zn concentrations were similar to Ba, with highest values at PF400 or PF600N, but there were no obvious differences in concentrations between sampling periods as seen for Ba. Ni concentrations, in contrast to Ba and Zn, were

maximal at PF600N in the February 1989 and October 1989 and remained relatively constant otherwise, suggesting an alternate source of Ni near the PF600N site, not associated with the produced water discharges.

5.5.2.2 Vertical Profiles

Vertical sediment core section samples for stations PF400, PF600N and PF800N from February 1989 were analyzed for trace metals because these stations showed uniform, down core contamination with petroleum hydrocarbons as evidenced by the FFPI values (Figure 5.19). Figure 5.23 shows the depth profiles for Ba, Zn and Ni concentrations, and the data are detailed in Tables E.16 - E.18. These metals showed the highest concentrations of all metals when summed over all surface stations within each collection period. In general, Ba concentrations, and Zn concentrations to a lesser degree, followed a pattern similar to that of the hydrocarbon data.

PF400: The pattern seen in this core for Ba and Zn is similar to the pattern of total hydrocarbons, with a minimal value in the 15-20 cm section. Highest metal concentrations, 660 ppm Ba and 170 ppm Zn, were found in the top sections of the core. Ni concentrations averaged 25 ppm throughout the core.

PF600N: Concentrations of Ba and Zn again followed a similar pattern to hydrocarbon data in this core, with a surface maximum followed by a secondary peak between 15 and 25 cm. In contrast to the hydrocarbon data, however, these trace metals were approximately double the concentrations found in PF400. The depth profile for Ni shows a significant increase in the 2-5 cm section, that represents the highest value, 430 ppm, found in all Pass Fourchon samples analyzed. The surface section showed 150 ppm of Ni, the next highest value, and similar to the value found at the surface in the October collection at PF600N.

PF800N: Again similar to hydrocarbon data, this core showed a pattern of decreasing Ba concentrations with depth, with a high value of 1,000 ppm at the surface, dropping to a minimum of 200 ppm in the 30-38 cm region. Zn concentration remained stable at approximately 130 ppm throughout the core, while Ni concentrations were minimal throughout except for a high value of 63 ppm in the 15-20 cm section.

5.5.3 Radionuclides

5.5.3.1 Surficial Sediments

Surficial sediment Pb-210 concentrations in the Pass Fourchon study area exhibited similar spatial patterns for each of the four sample periods (Figure 5.24, Table F.5). Pb-210 activities were highest in surface sediments at PF400 and decreased uniformly away from the discharge site. Surface Pb-210 activities ranged from 0.61 to 7.09 dpm·g⁻¹ during February 1989, from 1.03 to 6.69 dpm·g⁻¹ during May 1989, from 0.66 to 4.12 dpm·g⁻¹ during October 1989 and from 0.50 to 4.99 dpm·g⁻¹ during February 1990. Surface sediment Pb-210 activities correlated with percent organic carbon content and, to a lesser extent, with grain size, in particular, clay content (Figure 5.25). These correlations are expected due to the surface sorption reactions that govern Pb-210 chemical behavior. The quality and quantity of particle surface sites available for Pb-210 sorption is determined largely by grain size and organic content. Surface sediment Pb-210 activities in coastal environments are typically about 2.0 dpm·g⁻¹ (range: 0.1 to 5.0 dpm·g⁻¹), depending on many factors controlling the sorption reactions (e.g., grain size, percent organic carbon, turbidity in overlying waters). The surface sediment Pb-210 activities observed at Pass Fourchon were at or above the upper limit for activities found in natural environments.

5.5.3.2 Vertical Profiles

Sediment Pb-210 activities within the upper 10-50 cm (length of the cores collected) increased or remained the same in a down-core direction (Figure 5.26). This is different from natural environments where Pb-210 sediment activities decrease down core due to decay and reach a constant background level (~ 0.1 to $0.5 \text{ dpm}\cdot\text{g}^{-1}$). Decreasing Pb-210 activities with depth in the core is a prerequisite for calculating sedimentation rates; since these conditions were not present, sedimentation rates could not be calculated for Pass Fourchon (see Section 3.6). The pattern observed in cores at Pass Fourchon indicated that Pb-210 supply to the sediments has greatly exceeded decay. Because the Pb-210 activities do not decrease to a background level in the Pass Fourchon cores, the inventories calculated from these cores give a minimum estimate of the Pb-210 flux to the area. During February 1989, minimum Pb-210 sediment inventories ranged from 38.1 to 275.5 $\text{dpm}\cdot\text{cm}^{-2}$ (Table F.6). These inventories indicate Pb-210 fluxes of more than 1.2 to 8.5 times greater than natural supply. During May 1989, minimum Pb-210 sediment inventories ranged from 44.2 to 279.0 $\text{dpm}\cdot\text{cm}^{-2}$, indicating fluxes of more than 1.3 to 8.6 times greater than natural supply (Table F.7). During October 1989, minimum Pb-210 sediment inventories ranged from 19.0 to 136.0 $\text{dpm}\cdot\text{cm}^{-2}$, indicating fluxes of more than 1.0 to 4.2 times greater than natural supply. During February 1990, minimum Pb-210 sediment inventories ranged from 2.5 to 147.6 $\text{dpm}\cdot\text{cm}^{-2}$, indicating fluxes of more than 1.0 to 4.6 times greater than natural supply.

5.6 Benthic Biota

The benthic infauna of the Pass Fourchon study area was composed primarily of polychaetes, with *Streblospio benedicti* being dominant. Another polychaete opportunist, *Mediomastus ambiseta*, was common in the May 1989 collections. The bivalve, *Mulinia lateralis*, was numerous during February 1990 and was common during the other sample dates. The benthic fauna included additional polychaete species, a few bivalves and gastropods, nemertean worms, oligochaetes and pericaridean crustaceans.

There were notable differences in the benthic communities of those stations within 800 m of the discharge. Benthic infauna was absent or substantially reduced at 400, 500, 600 and 800 m from the discharge point for most of the sample periods (Table G.1, Figures 5.27 - 5.28). Depending upon the positioning of the ship in the dead-end channel, benthic infauna was absent or reduced at PF600N and/or PF800N. Infauna was reduced in the deeper parts of the channel where the effluent density plume followed the bottom contours, but was present at higher topographic locations not impacted by the bottom-hugging effluent. The benthic fauna at PF600S and at distances of greater than 800 m to the north was not impacted by the discharges.

There were significant differences among stations for most benthic community parameters for all sample dates (Tables 5.3 - 5.6, Tables G.2 - G.5) and for the interaction of station and sample date (Table 5.7, Table G.6). It should be noted that very often cell sizes were unequal or stations completely excluded from analyses of variance of the diversity and evenness parameters because of missing values or zero values for all replicates. In these cases, only the remaining values were used in the analyses, and the results were biased by the exclusions.

In February 1989, there were significantly fewer species and number of individuals at stations PF400 and PF800N. During this collection period, station PF600N was more similar to PF600S. In May 1989, stations PF400, PF500S, PF500N, PF600N and PF800N had significantly fewer species and individuals than the other stations. In October 1989, stations PF400, PF600N and PF800N were most similar to each other with fewer species and individuals. In February 1990, there were significantly fewer species and number of individuals at stations PF400 and PF600N.

With benthic data combined in a co-analysis of variance of sample date, station and their interaction, it was clear that station PF400 had significantly fewer species and individuals than the remaining stations (Table 5.7, Table G.6). There were also significant differences between stations PF600N and PF800N and the remainder of the stations for number of species and individuals. There were differences in benthic communities based on the date of sampling, but the significance of the reduced fauna at PF400, PF600N and PF800N was evident regardless of sample date. There were more species collected during February of both 1989 and 1990 than in the other collection periods, but there were no differences between the years (Table 5.7). The number of individuals during the recruitment period of February in 1990 was significantly greater than the same month of 1989. The increase in number of individuals in February 1990 was due to the presence of the polychaete, *Streblospio benedicti*. There were no differences in the number of individuals among all the stations for the remainder of the sample dates (Table 5.7). There were no differences among stations for the parameters of diversity and evenness by sample date.

There were relationships between the benthic community composition and the sedimentary environment of Pass Fourchon. The numbers of species and individuals were greater in sediments with a higher percent sand content. The number of species was reduced in those sediments with a higher total organic content. Organic content, however, was related to the grain size distribution as well as the level of chemical constituents. Number of individuals was not clearly related to the total organic content of the sediments.

There were obvious relationships between the number of species and individuals collected at a station to the amount of chemical constituents in near-bottom waters or surficial sediments. Examples of these relationships are given in Figure 5.29. Basically, where the chemical contaminants exceeded a threshold level, the numbers of benthic fauna were either severely depressed or absent. These levels are outlined in Table 5.8.

5.7 Summary

The Pass Fourchon study area is a poorly flushed dead-end canal system which at the time of the field studies received a combined volume of $48,000 \text{ bbl}\cdot\text{d}^{-1}$ of produced water discharges. Current velocities within the canal system were low, consistently below $0.05 \text{ m}\cdot\text{s}^{-1}$. Flows were usually too low to calculate a shear velocity, but when sufficient, a calculated shear velocity of $0.88 \text{ cm}\cdot\text{s}^{-1}$ was probably insufficient to cause resuspension of bed material. Higher current velocities were observed in the main channel of Pass Fourchon, where there were also sandier surficial sediments than at the stations in the dead-end canal. Sandier sediments were also present at the 600S station nearest the beach environment. There was a notable change in the grain size distribution of the canal stations between May and October 1989, with a decrease in sand and an increase in silt.

A dense salinity plume could be identified as far as 800 m from the discharge point, but on one occasion was limited to 400 m. There were two instances of elevated sulfides in near-bottom waters. Consistent measurements of the extent of salinity differences and chemical contaminants in overlying waters and surficial sediments were hampered by the variability in the bottom topography of the dead-end canal. Deeper portions of the canal were not necessarily sampled for each collection. Stations at shallower water depths were less likely to be impacted by the density plume. Volatile organic hydrocarbons and PAH were detected in the near-bottom waters as far as 1000 m from the discharges but were most elevated to 800 m. Pb-210 and total radium activities in near-bottom waters were elevated above background levels 1000 m from the discharges as much as 5 to 42 times, respectively, above natural levels.

The PAH and total HC concentrations in surficial sediments were elevated above background levels as far as 800 m from the discharge point. The levels of hydrocarbons, relative

abundances of the alkylated PAH and the FFPI values indicate the produced water effluents as the source of the hydrocarbon constituents in the surficial sediments as far as 800 m from the discharge. Total PAH and saturated HC concentrations in surficial sediments for the stations within the dead-end canal were within the range of those for similar stations reported in Boesch and Rabalais (1989a). Pb-210 activities in surface sediments decreased uniformly away from the discharge site and were at or above the upper limit for activities found in natural environments. Temporal variability in the various chemical constituents of surficial sediments can be attributed to temporal variability in loading, treatment efficiency, sedimentological differences, spatial heterogeneity of the environment and variability in station location. Pb-210 vertical profiles indicated that the flux of Pb-210 to this environment far exceeded the natural decay rate. Vertical sediment cores analyzed for hydrocarbon constituents indicated substantial contamination with depths to 35 cm and a decrease in the overall vertical contamination with distance from the discharge. A severely depressed benthic fauna was indicative of elevated chemical constituents to a distance of 800 m from the discharge. Numbers of infaunal species and individuals increased at station PF600S and at 900 m or greater distance from the discharge. These distal stations were also characterized by different sedimentary characteristics and reduced concentrations of chemical constituents.

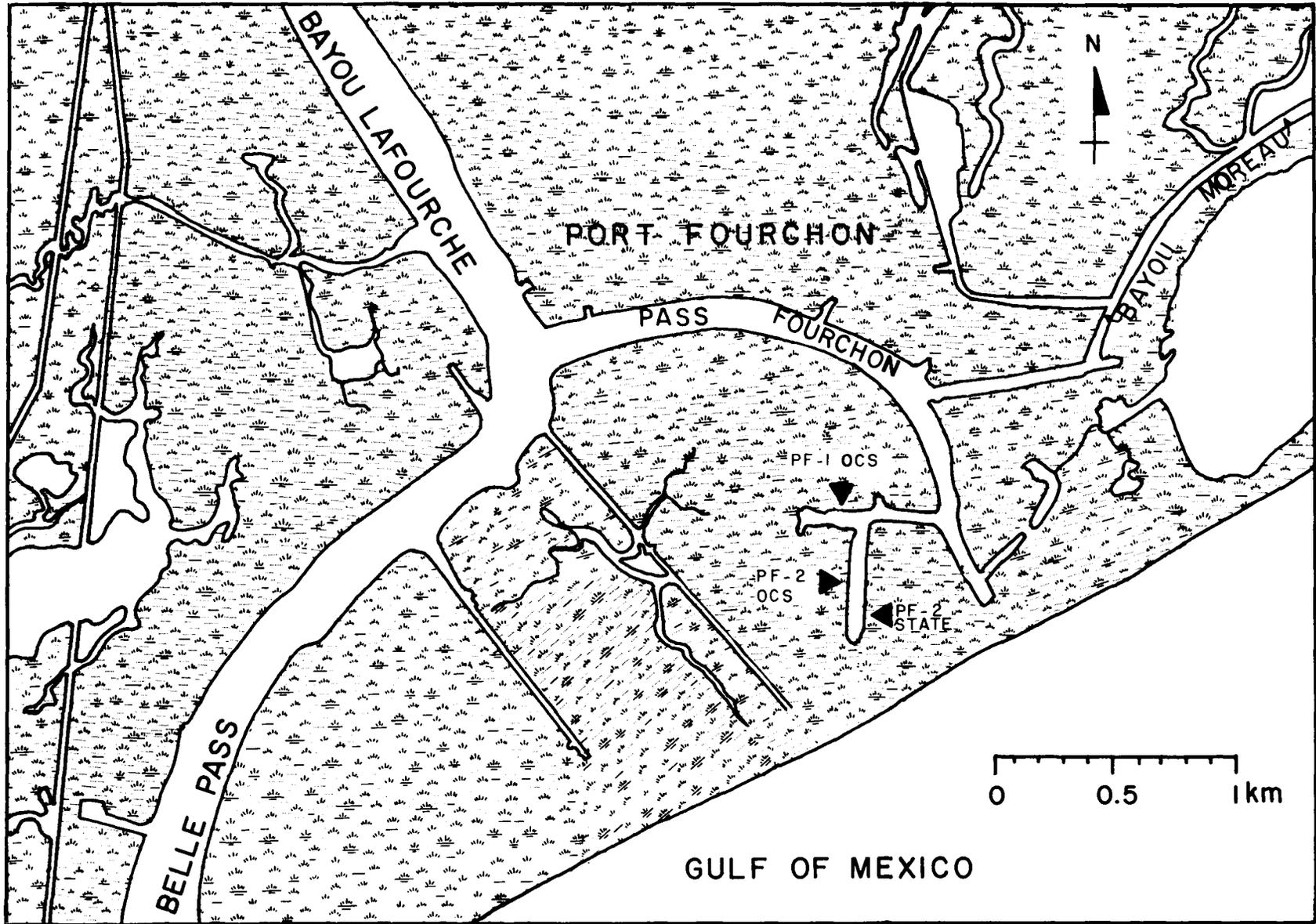


Figure 5.1. Pass Fourchon study area; produced water discharges indicated by closed triangles.

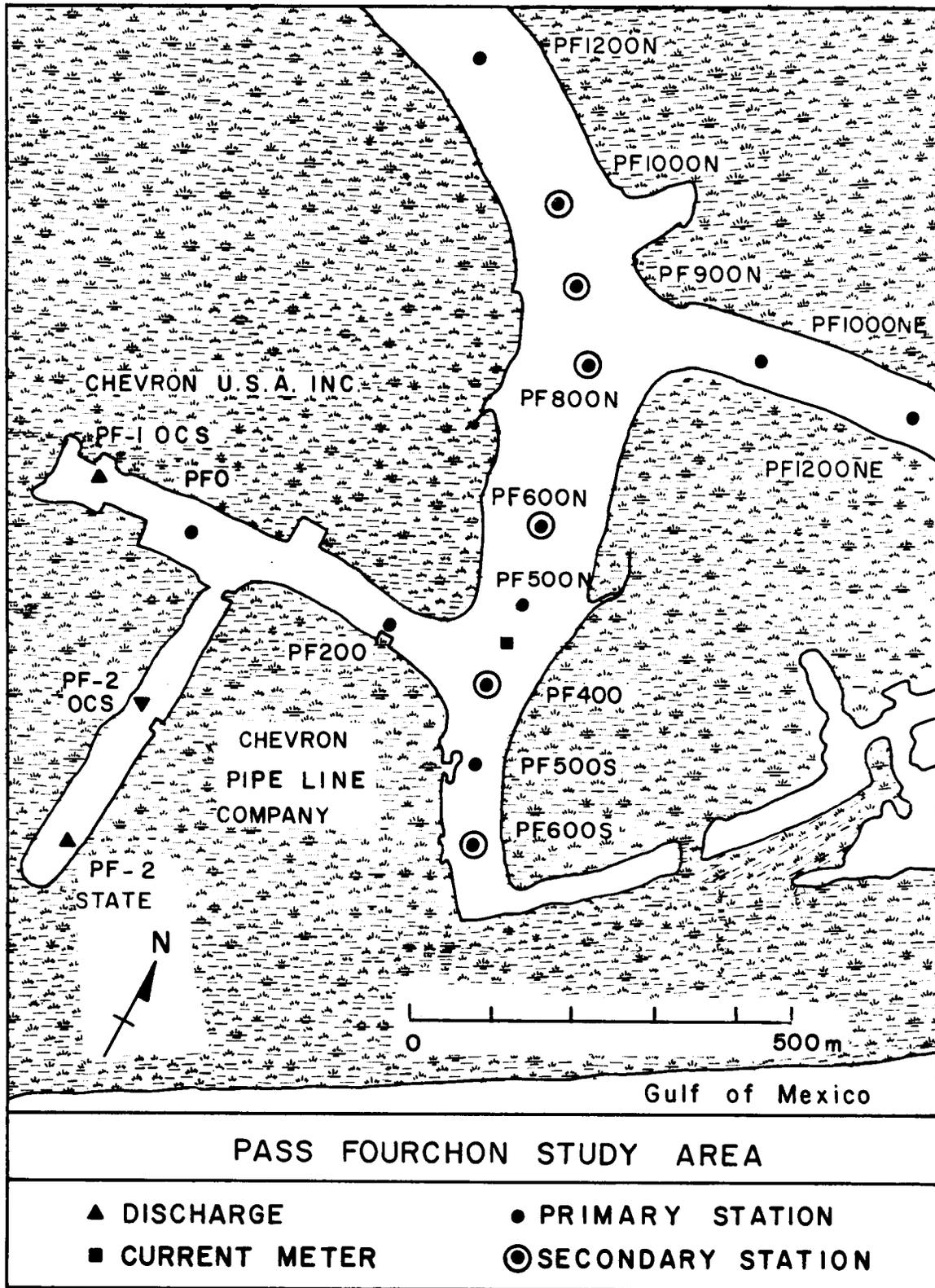


Figure 5.2. Location of stations at Pass Fourchon study area.

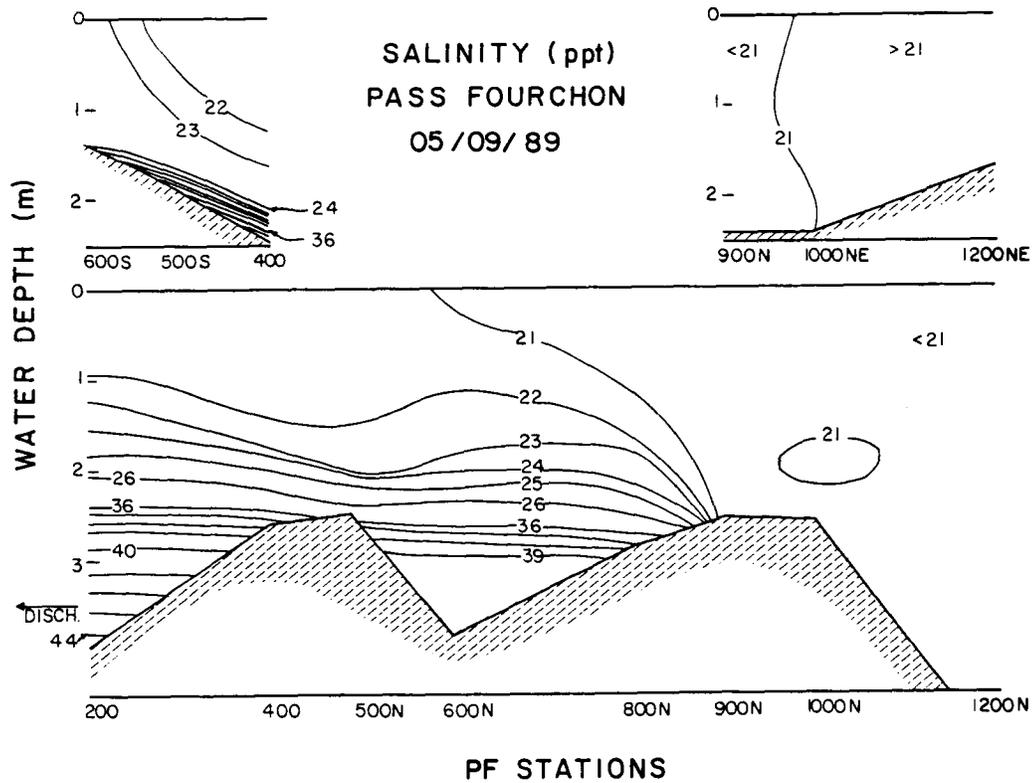
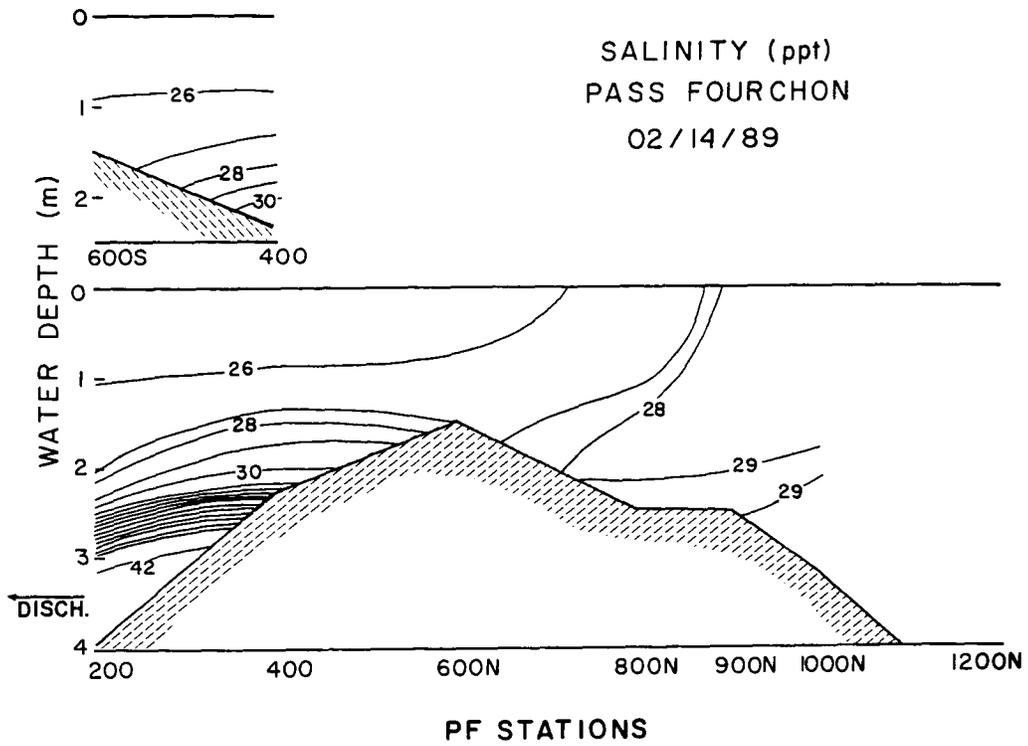


Figure 5.3. Salinity distribution through the water column at the Pass Fourchon study area, February and May 1989. DISCH. = direction of discharges.

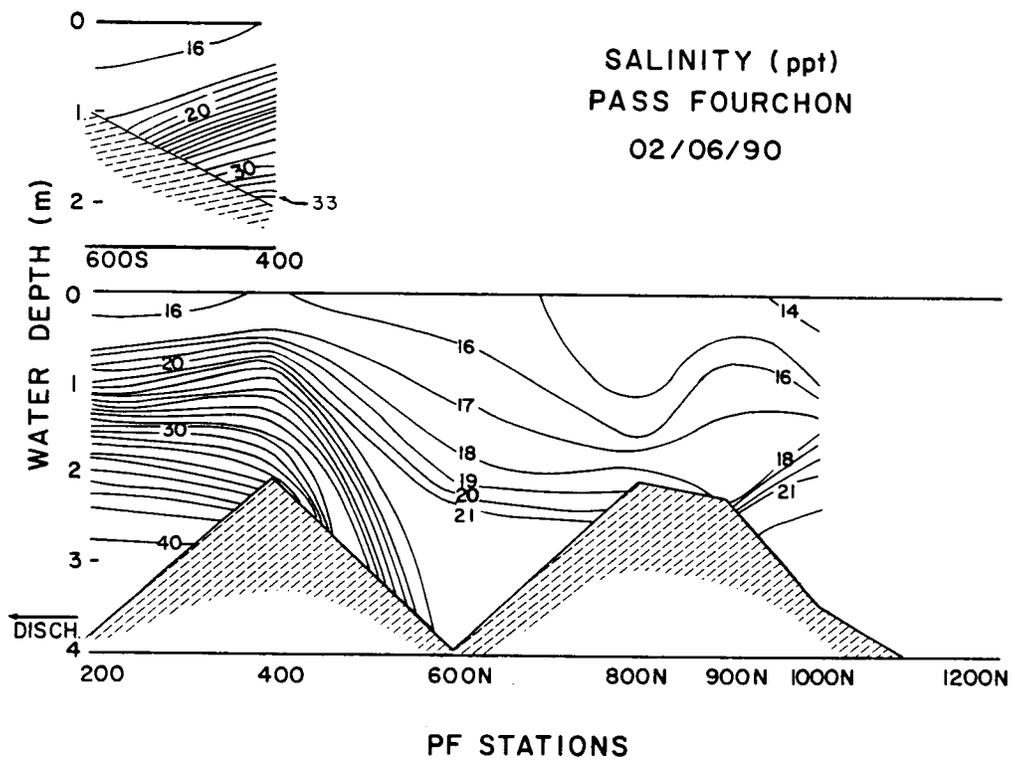
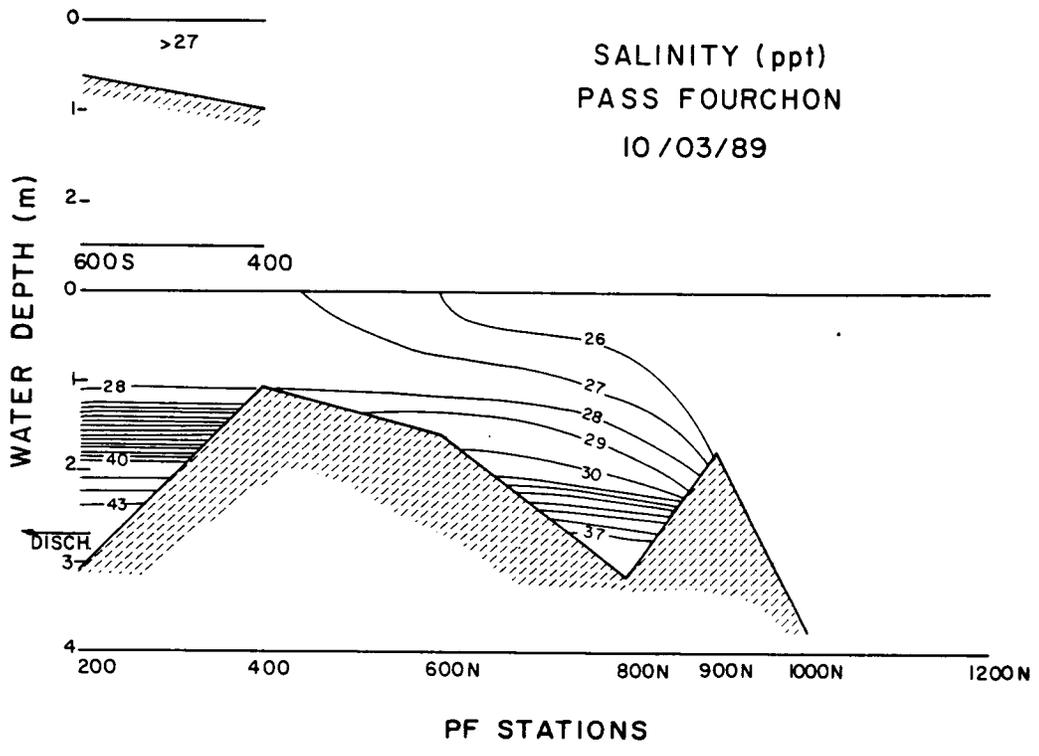


Figure 5.4. Salinity distribution through the water column at the Pass Fourchon study area, October 1989 and February 1990. DISCH. = direction of discharges.

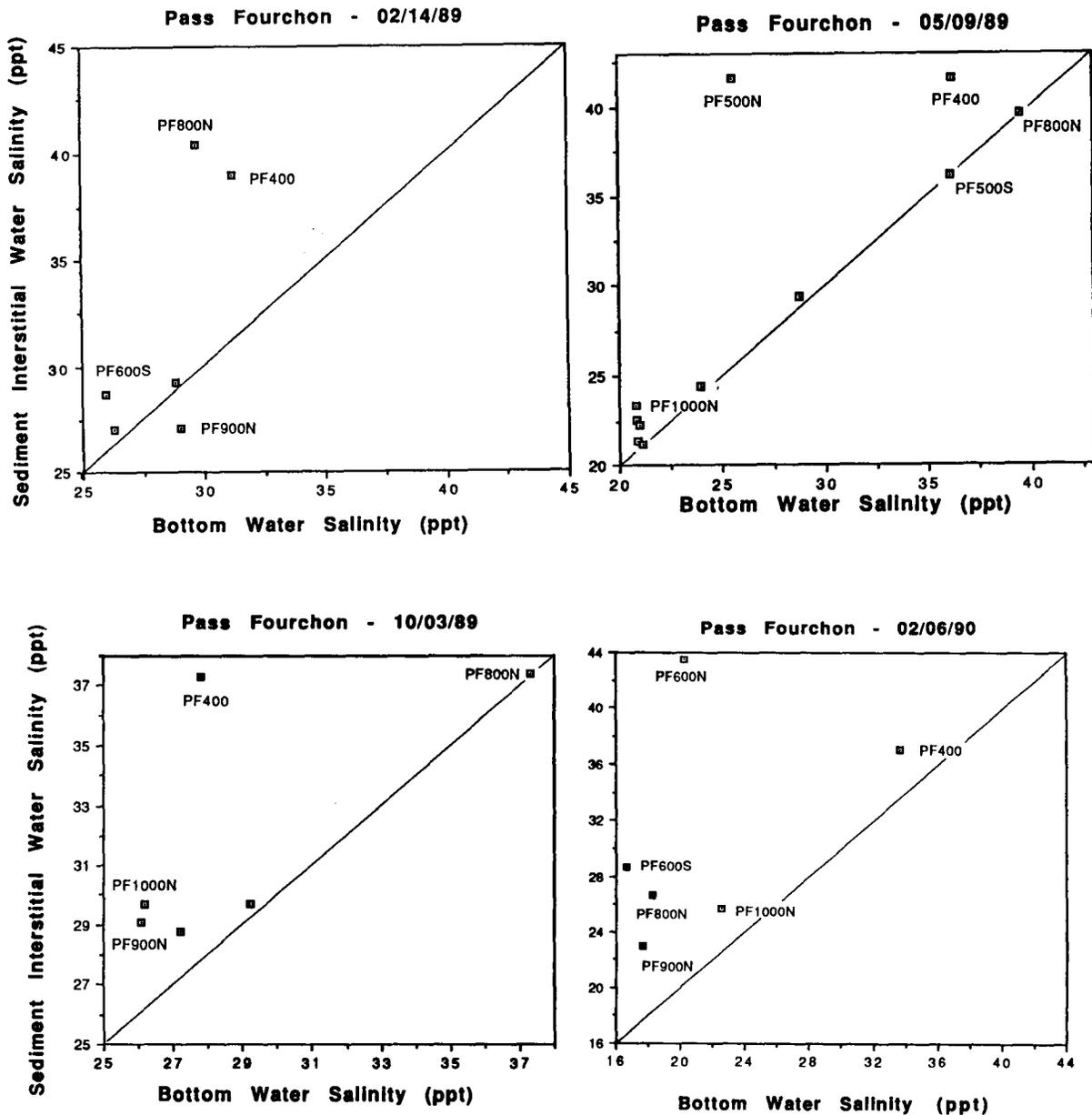
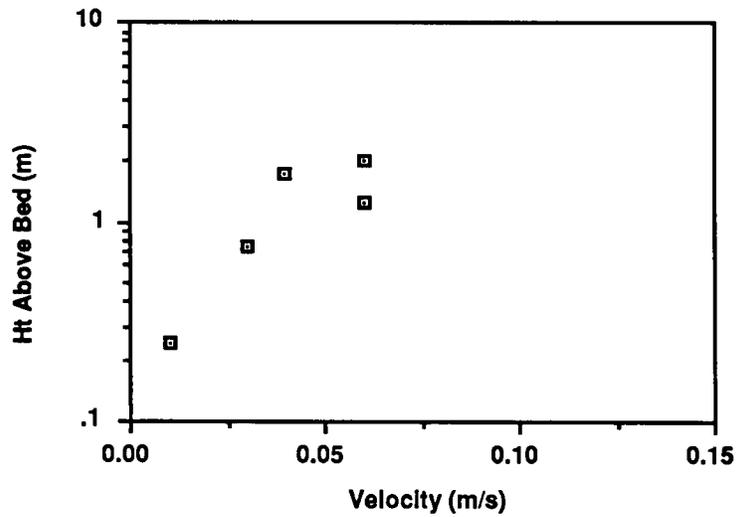


Figure 5.5. Comparisons of interstitial water salinity from surface sediments of stations in the Pass Fourchon Study area and near-bottom water salinity. Station number given for values most different from a 1:1 relationship (indicated by diagonal line) and/or for stations affected by density plume.



Location:	Pass Fourchon
Date:	9 May 1989
Time:	0900
Shear Velocity:	0.88 cm/s
Roughness Length:	15.68 cm
R-squared:	.773

Figure 5.6. Profile of current velocities through the water column at the Pass Fourchon study area for 9 May 1989 at 0900.

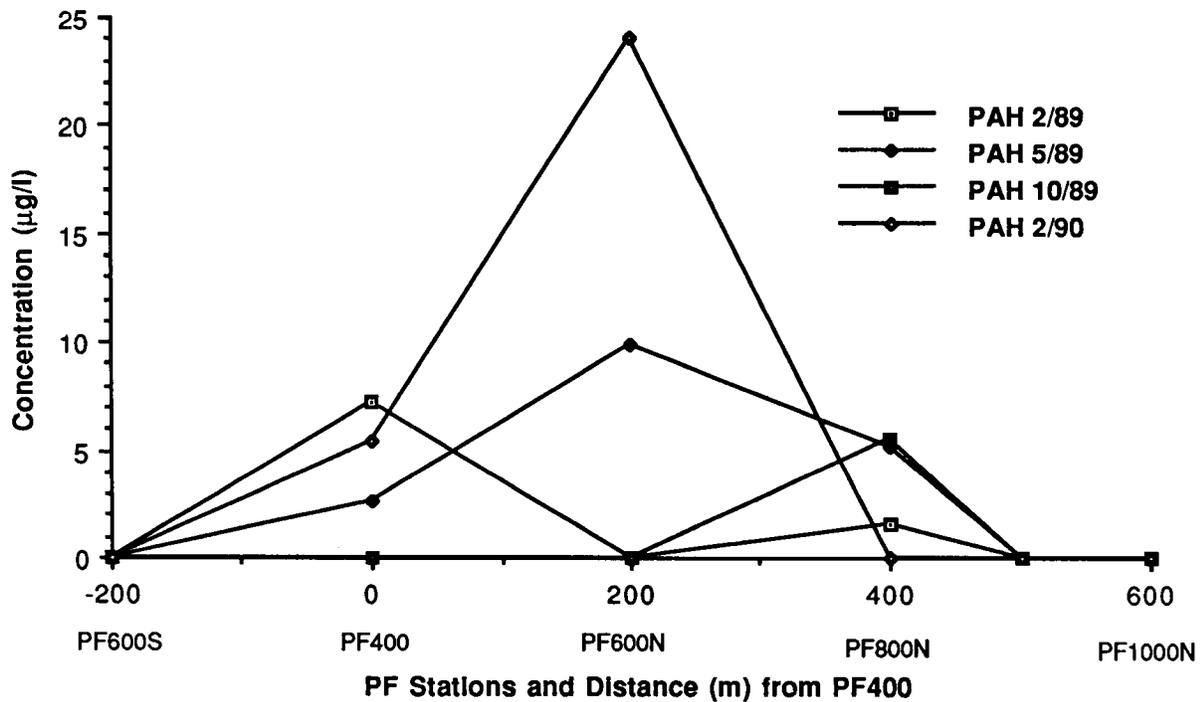
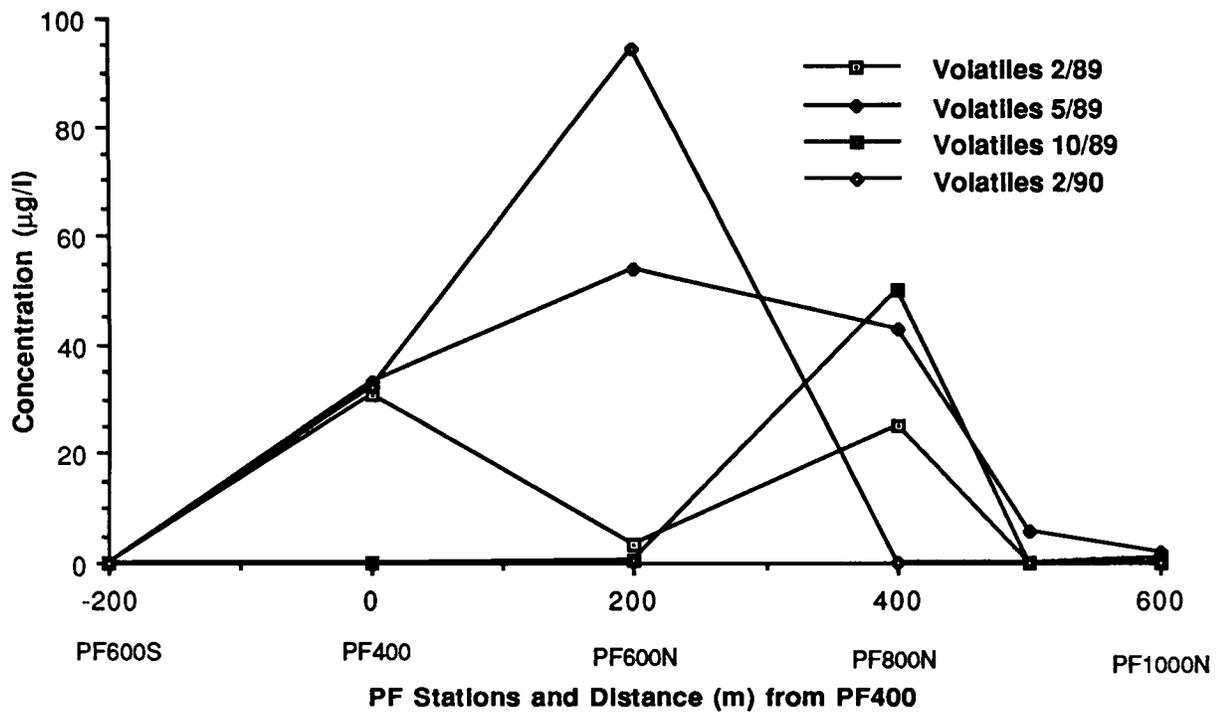


Figure 5.7. Spatial distribution of volatile hydrocarbon and PAH concentrations in Pass Fourchon near-bottom waters for four sample periods.

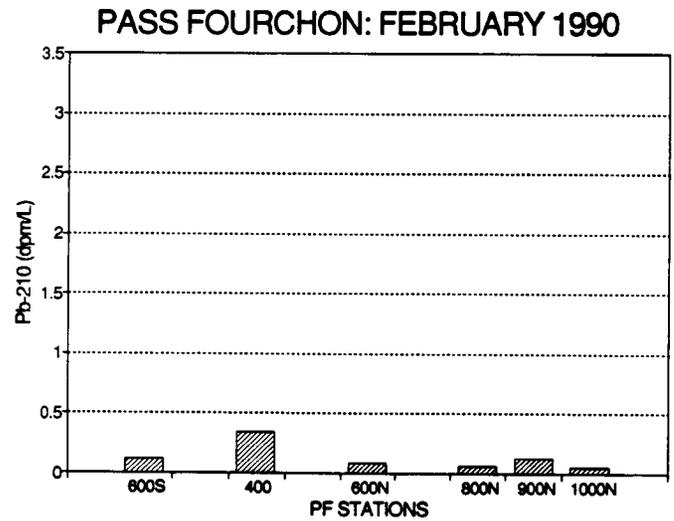
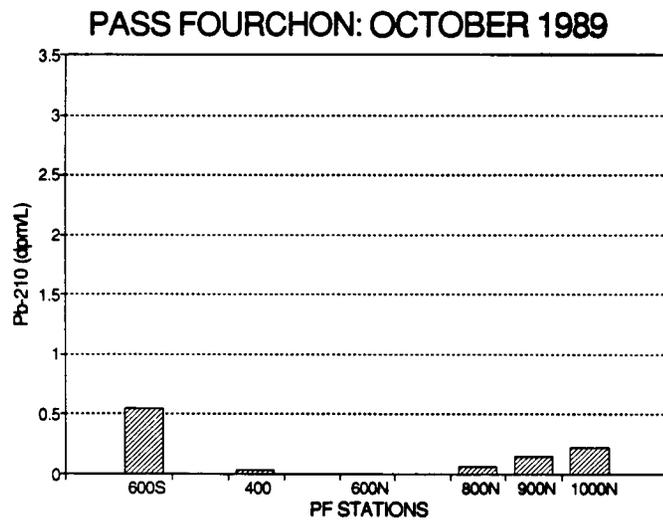
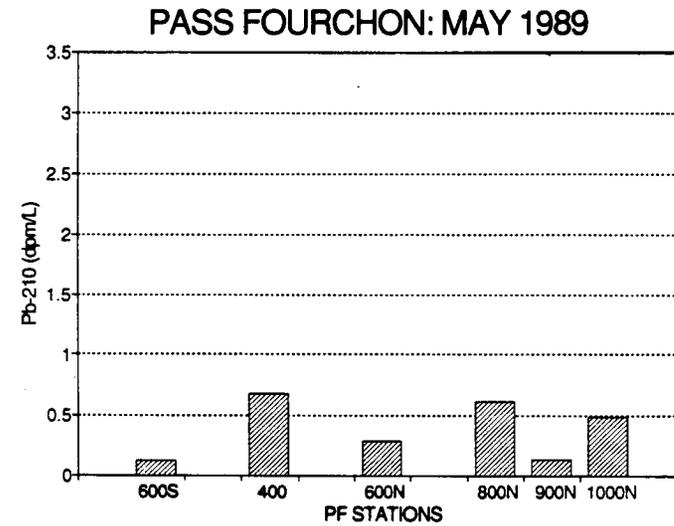
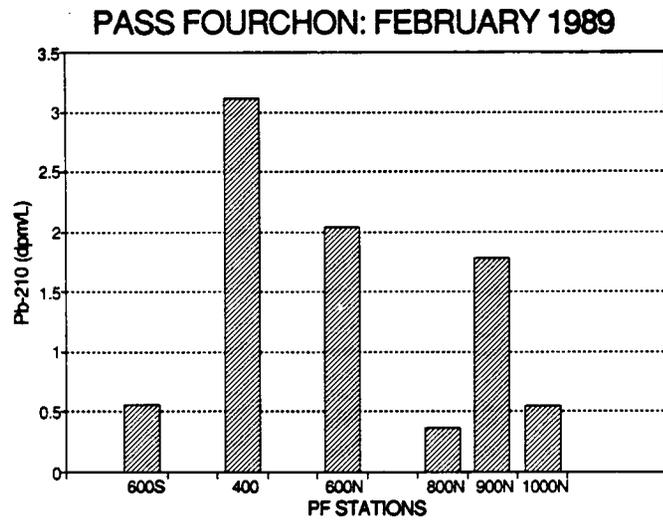


Figure 5.8. Spatial distribution of Pb-210 activities in Pass Fourchon near-bottom waters for four sample periods.

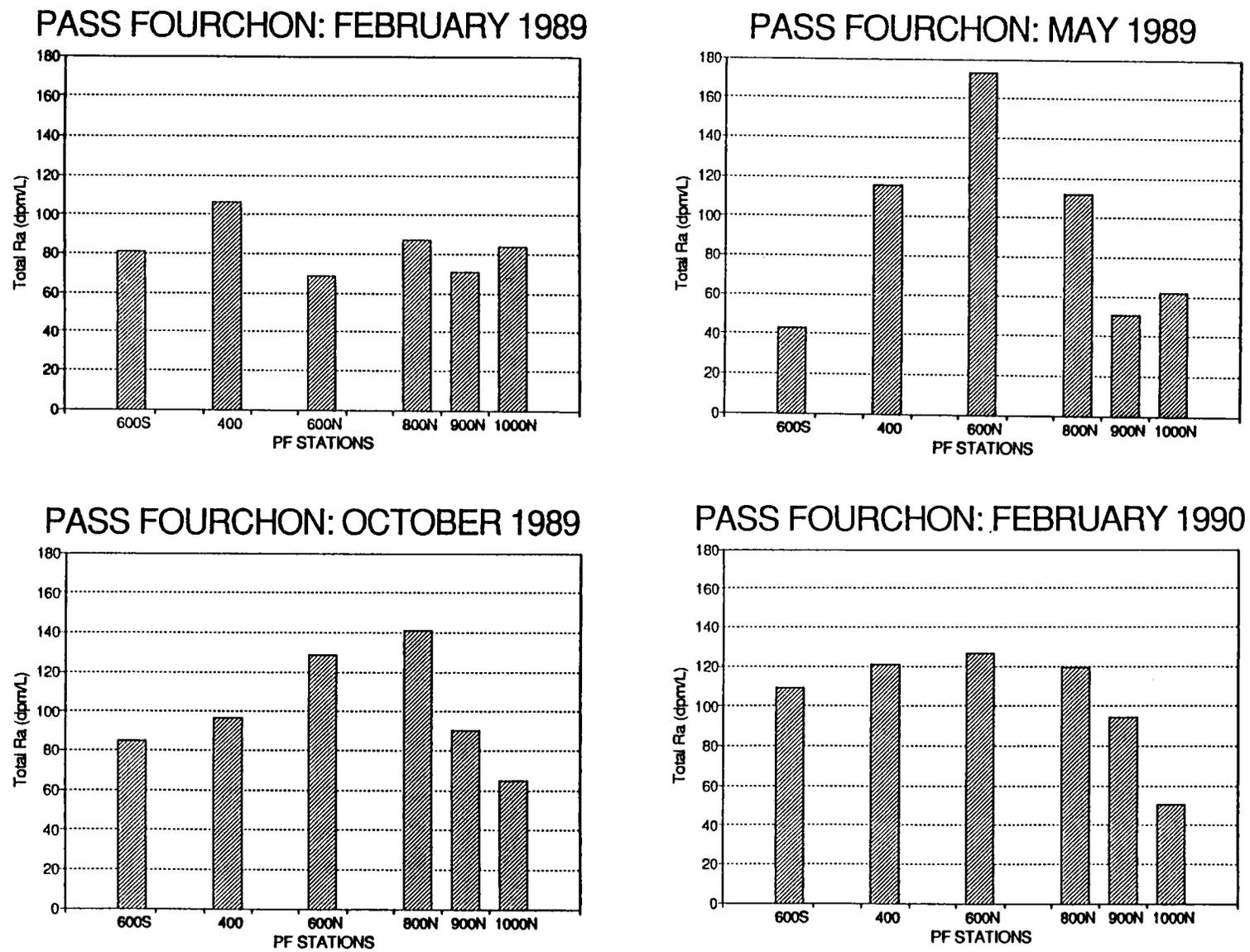


Figure 5.9. Spatial distribution of total radium activities in Pass Fourchon near-bottom waters for four sample periods.

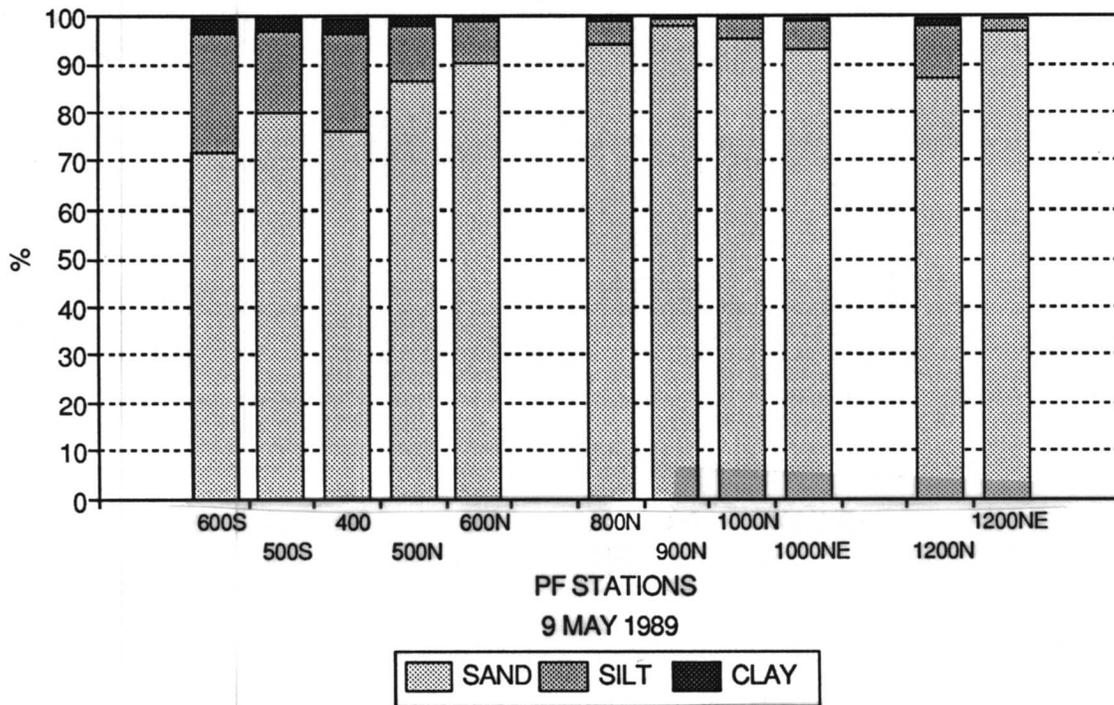
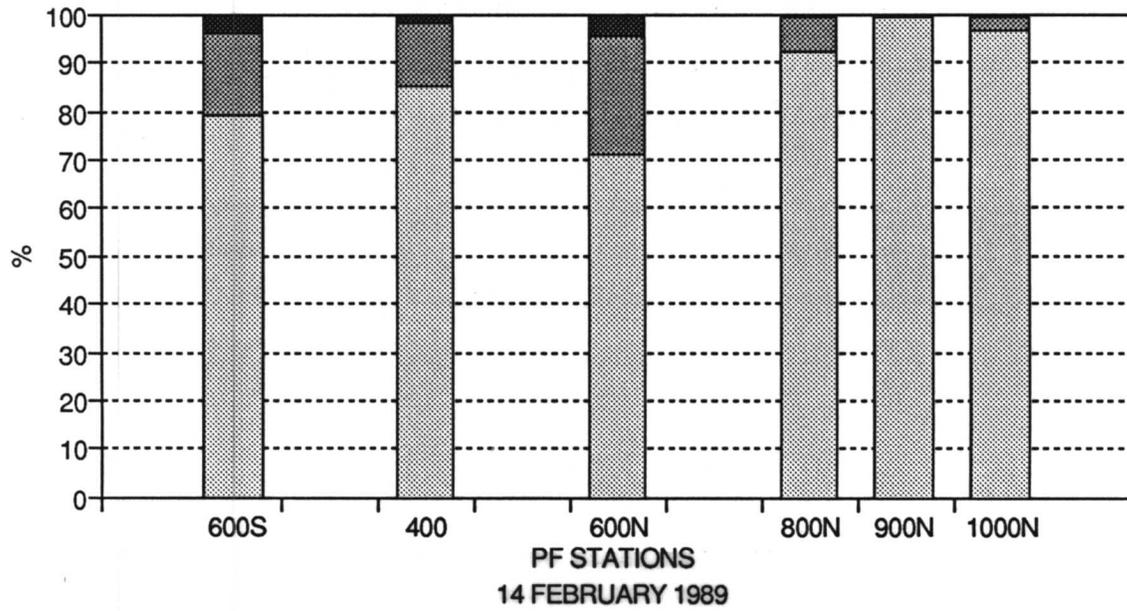


Figure 5.10. Spatial distribution of surface sediment grain size from Pass Fourchon, February and May 1989.

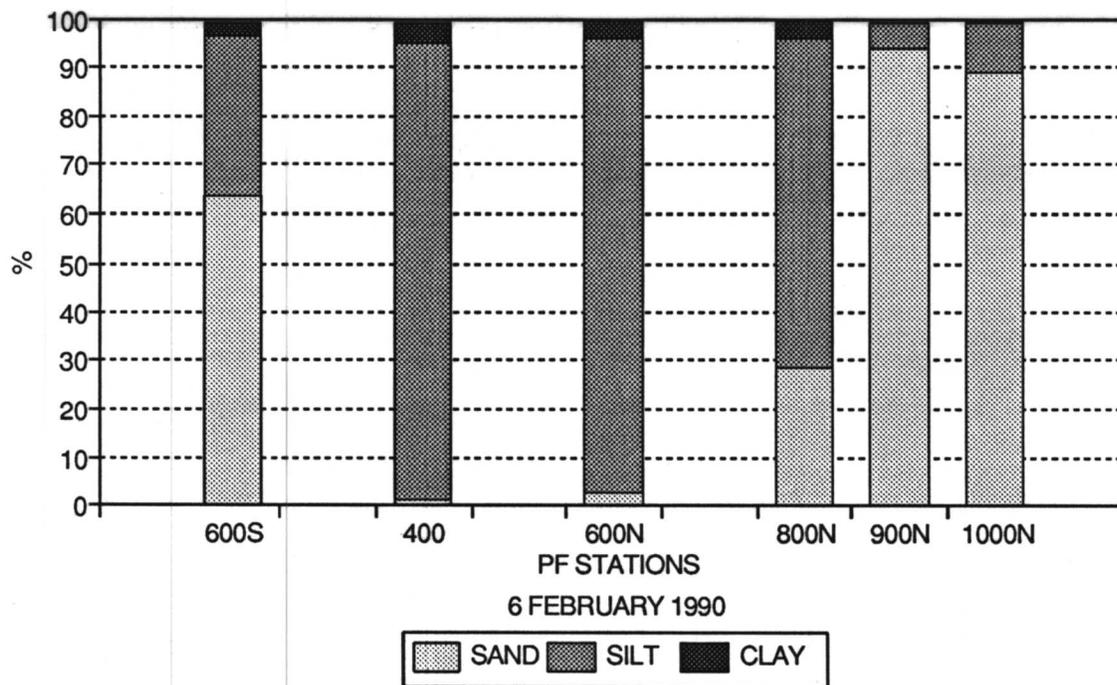
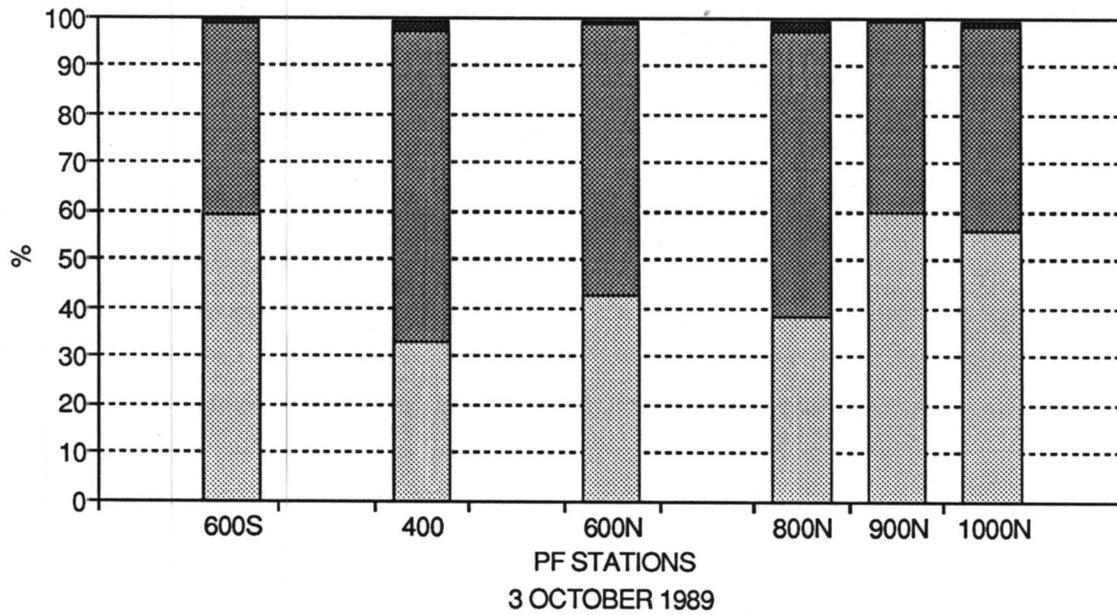


Figure 5.11. Spatial distribution of surface sediment grain size from Pass Fourchon, October 1989 and February 1990.

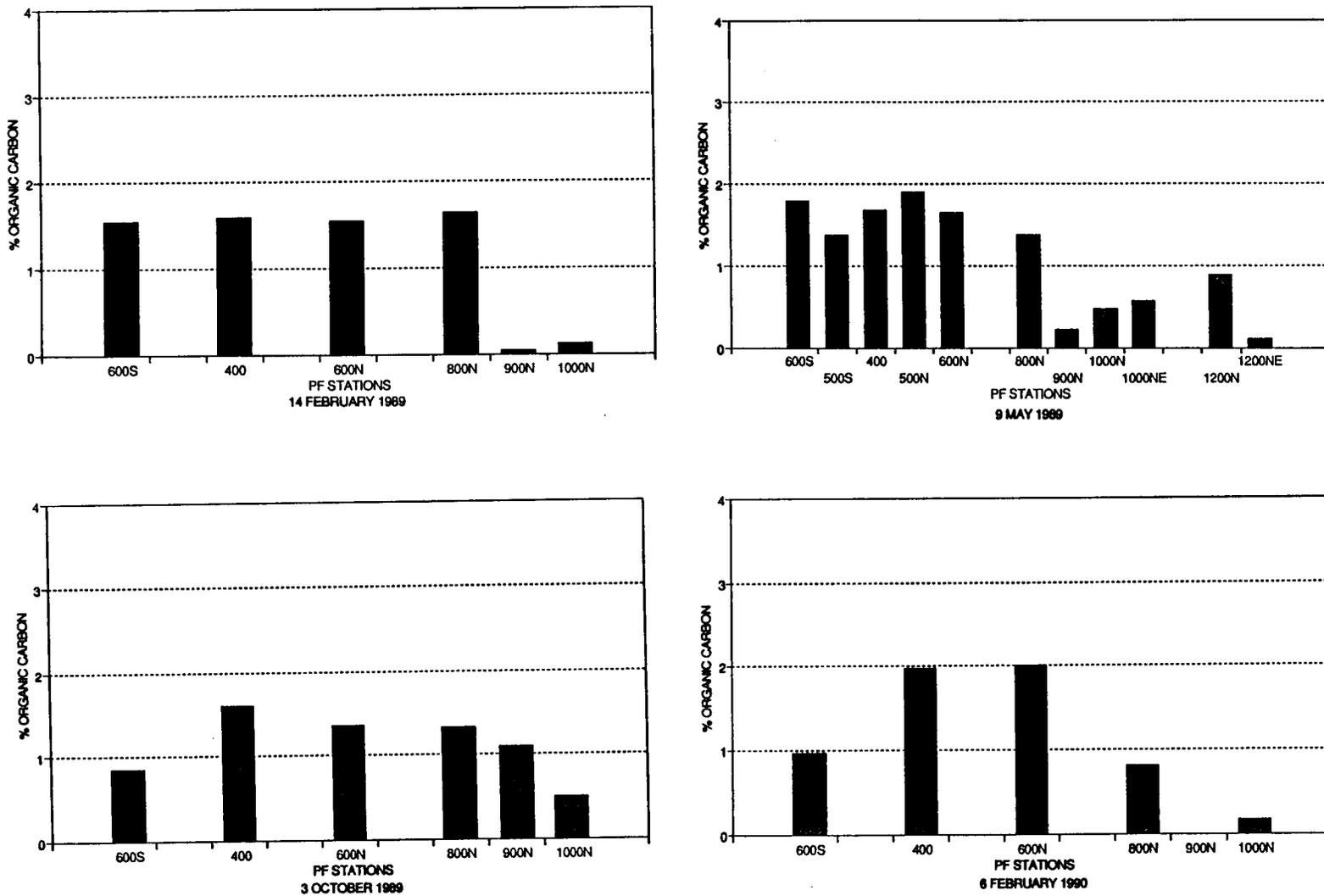


Figure 5.12. Spatial distribution of percent total organic carbon in surface sediments from Pass Fourchon for four sample periods.

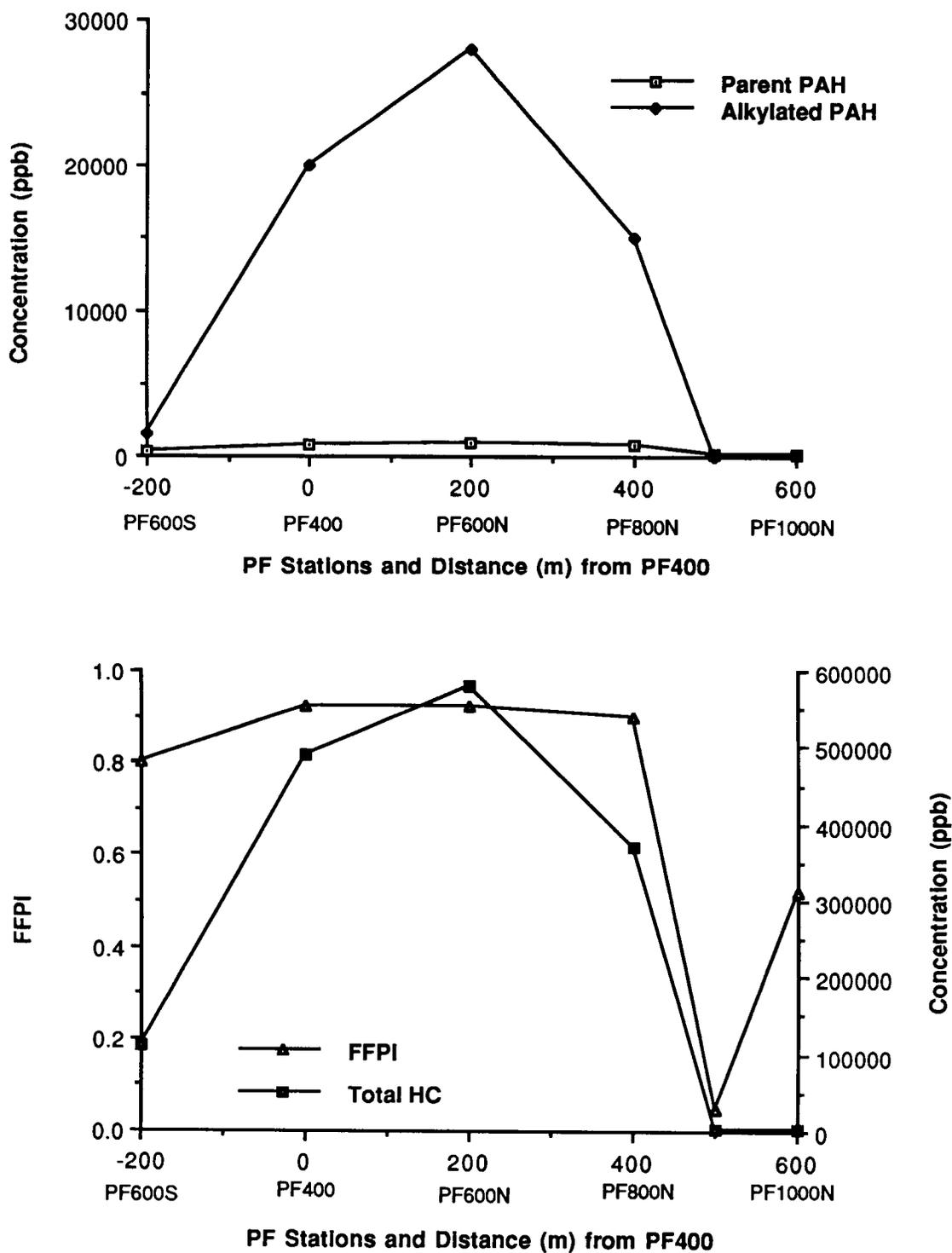


Figure 5.13. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from Pass Fourchon, February 1989.

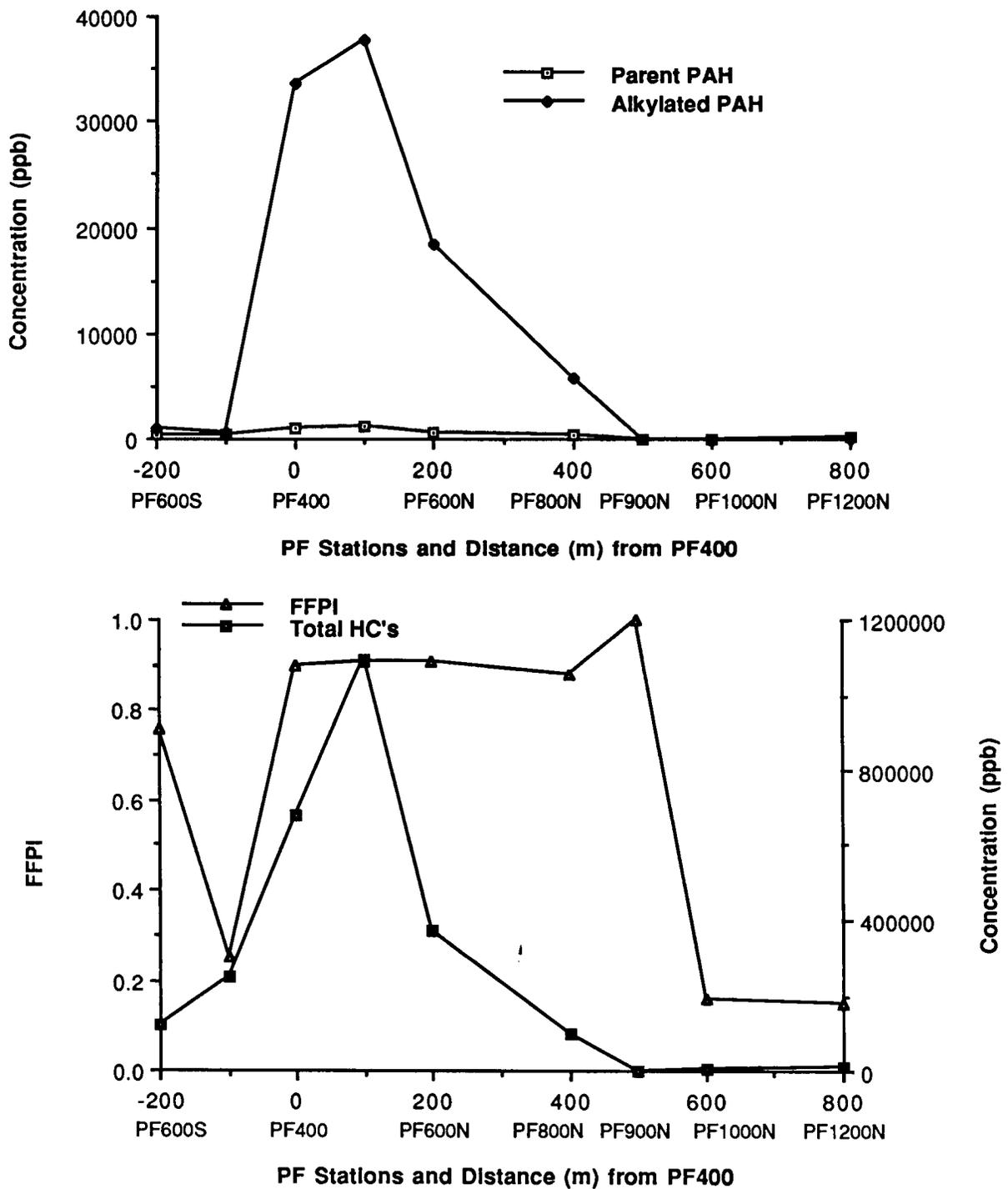


Figure 5.14. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from Pass Fourchon, May 1989.

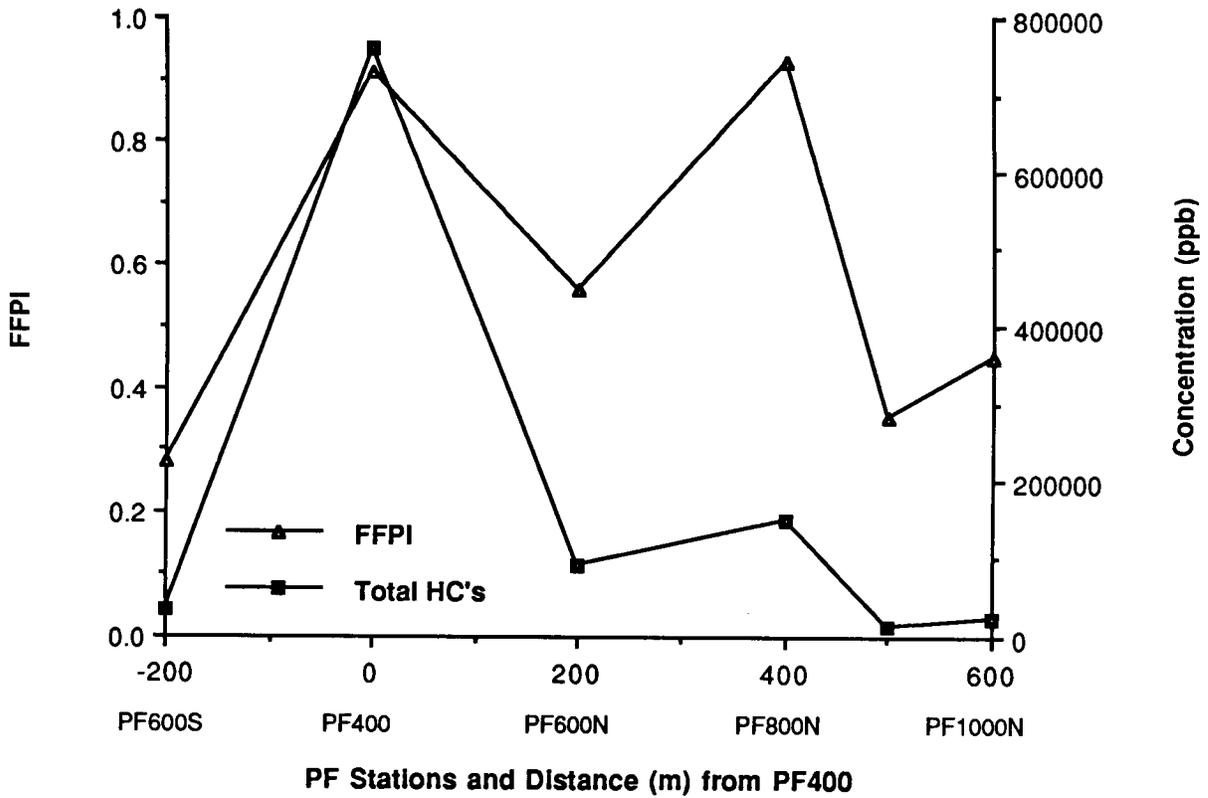
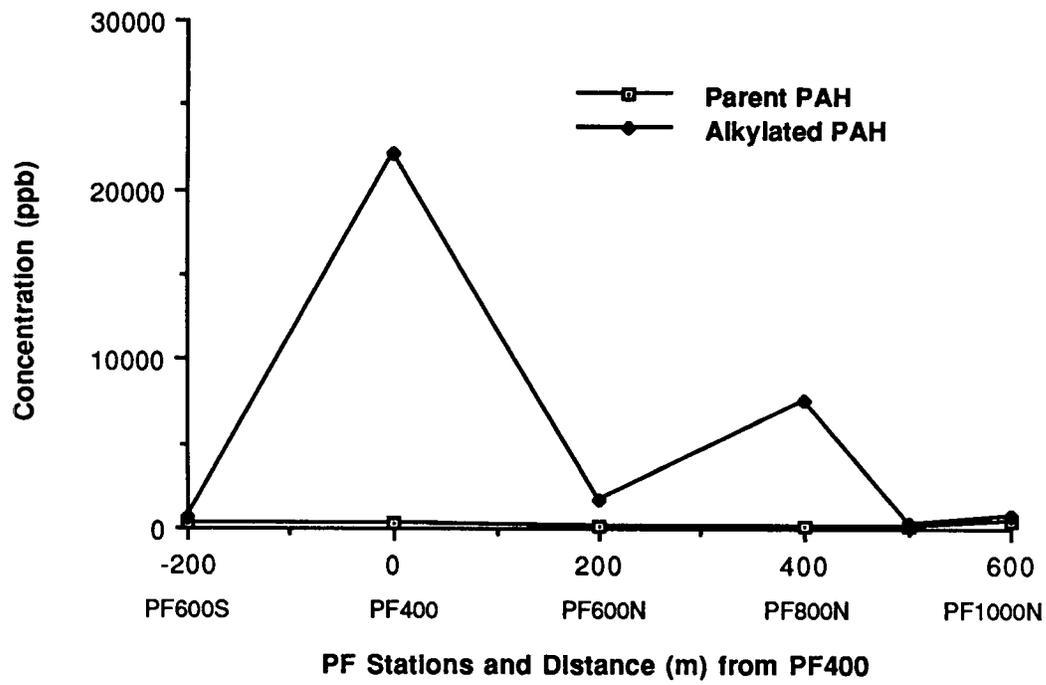


Figure 5.15. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from Pass Fourchon, October 1989.

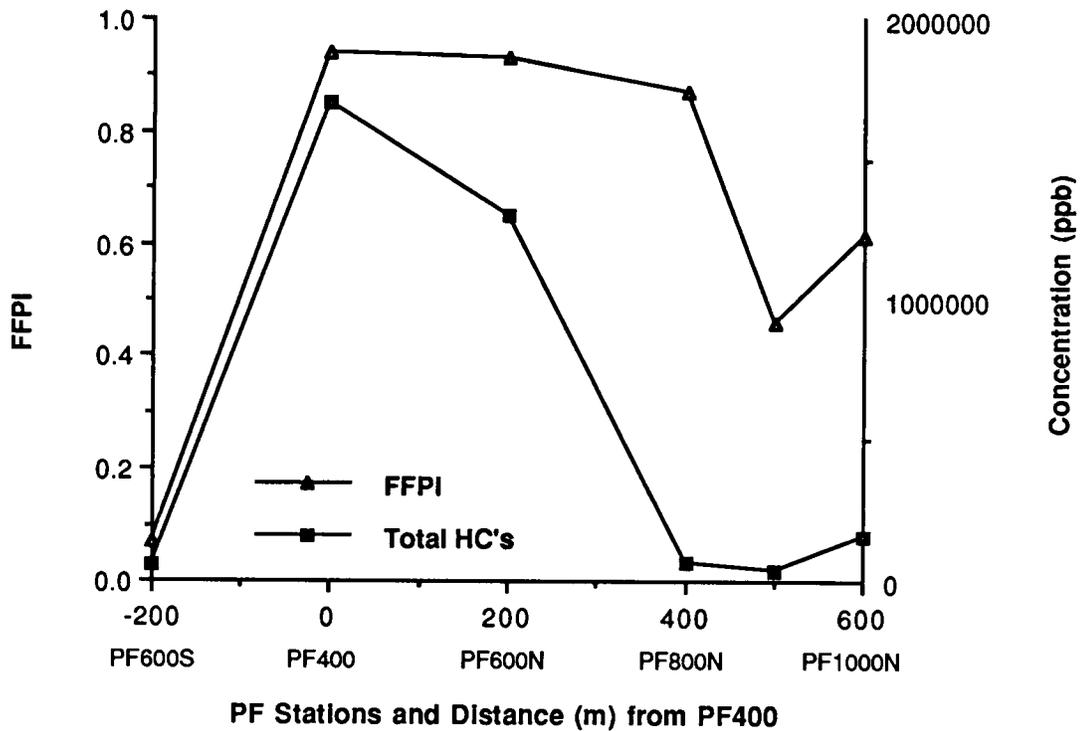
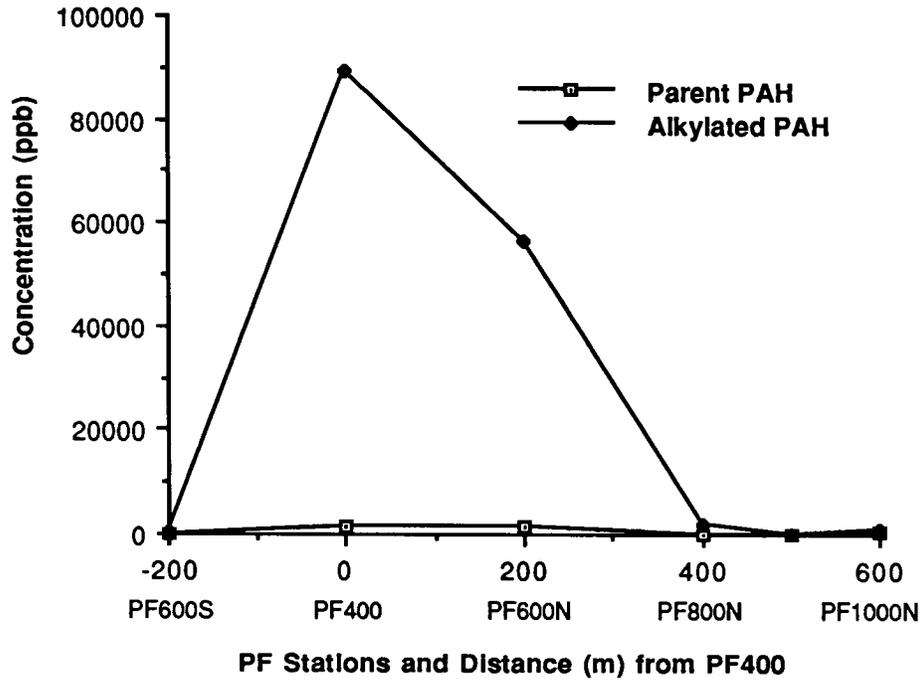


Figure 5.16. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from Pass Fourchon, February 1990.

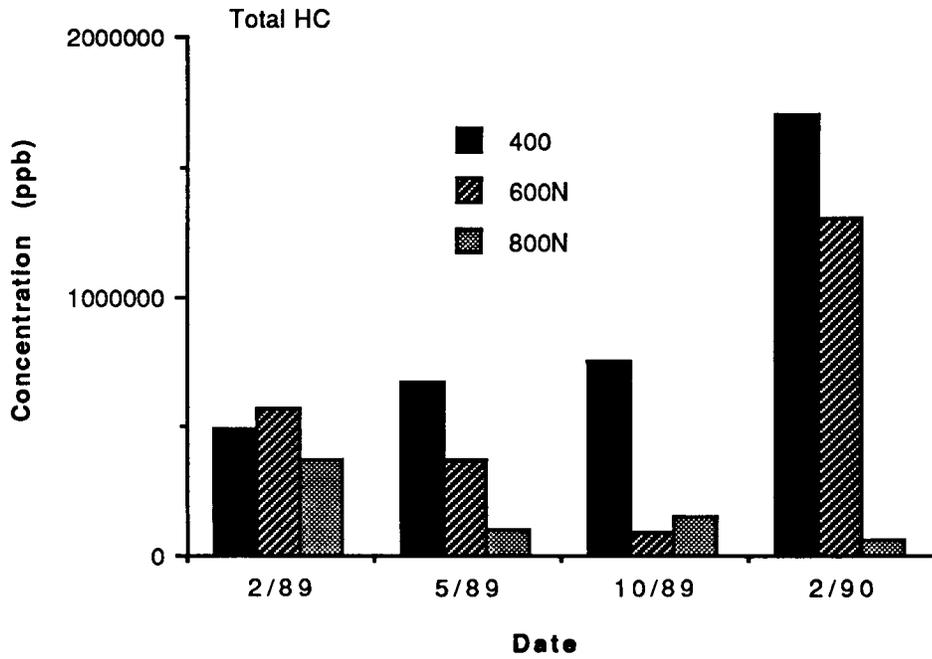
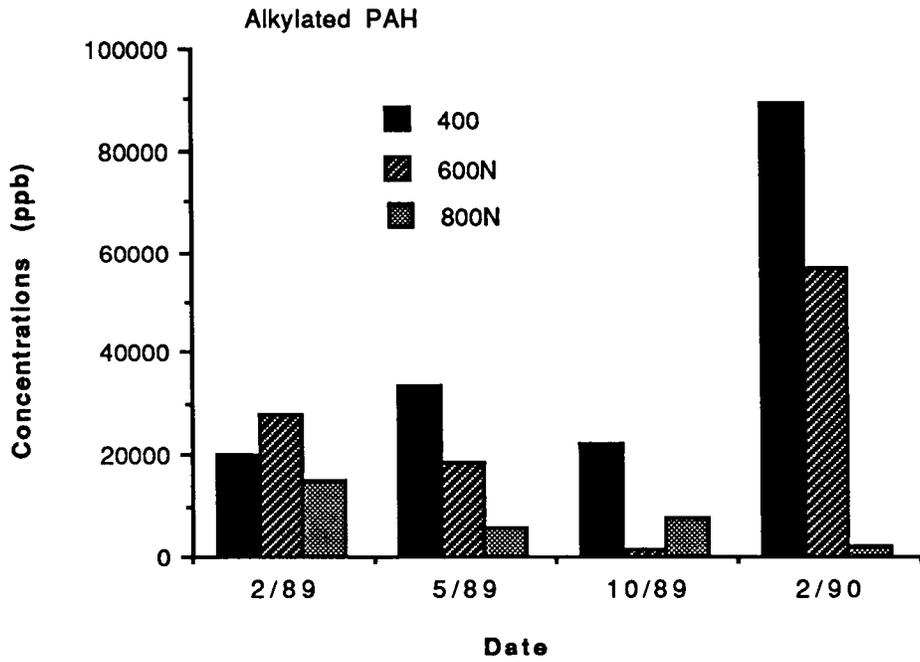


Figure 5.17. Temporal distributions of alkylated PAH and total HC concentrations in surface sediments from selected stations at Pass Fourchon.

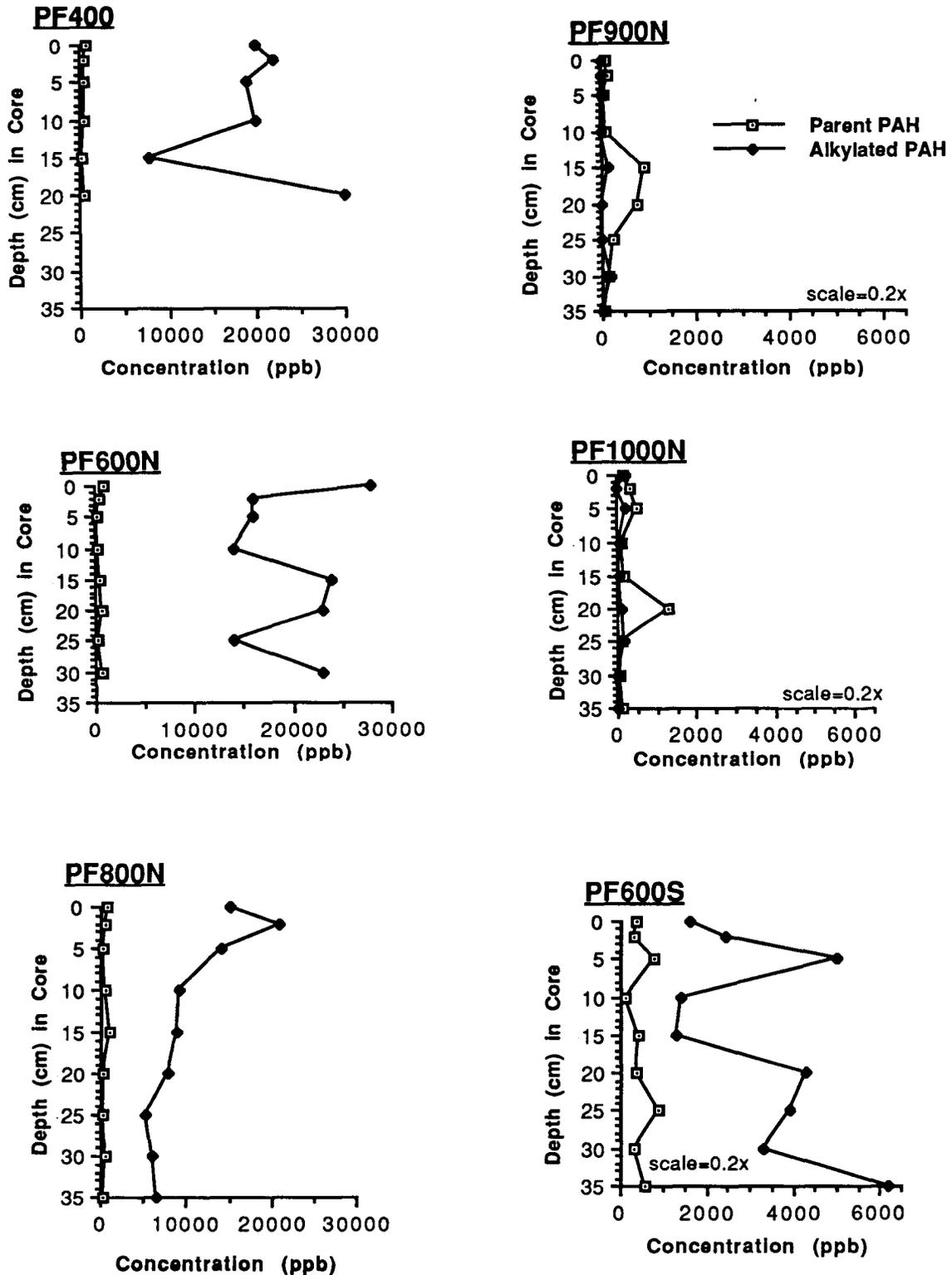


Figure 5.18. Total parent and alkylated PAH concentrations in vertical sediment core sections from Pass Fourchon, February 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

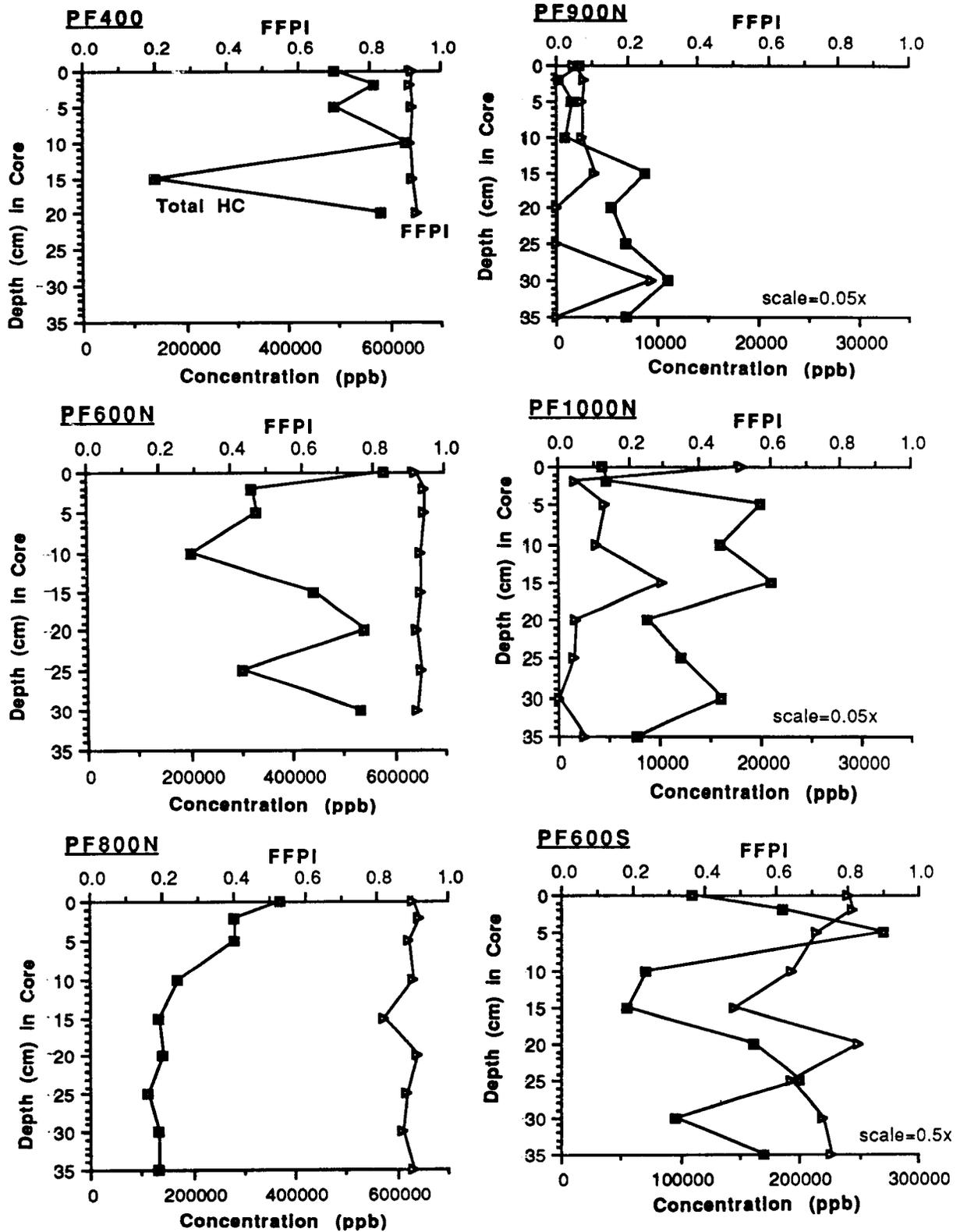


Figure 5.19. FFPI and total HC concentrations in vertical sediment core sections from Pass Fourchon, February 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

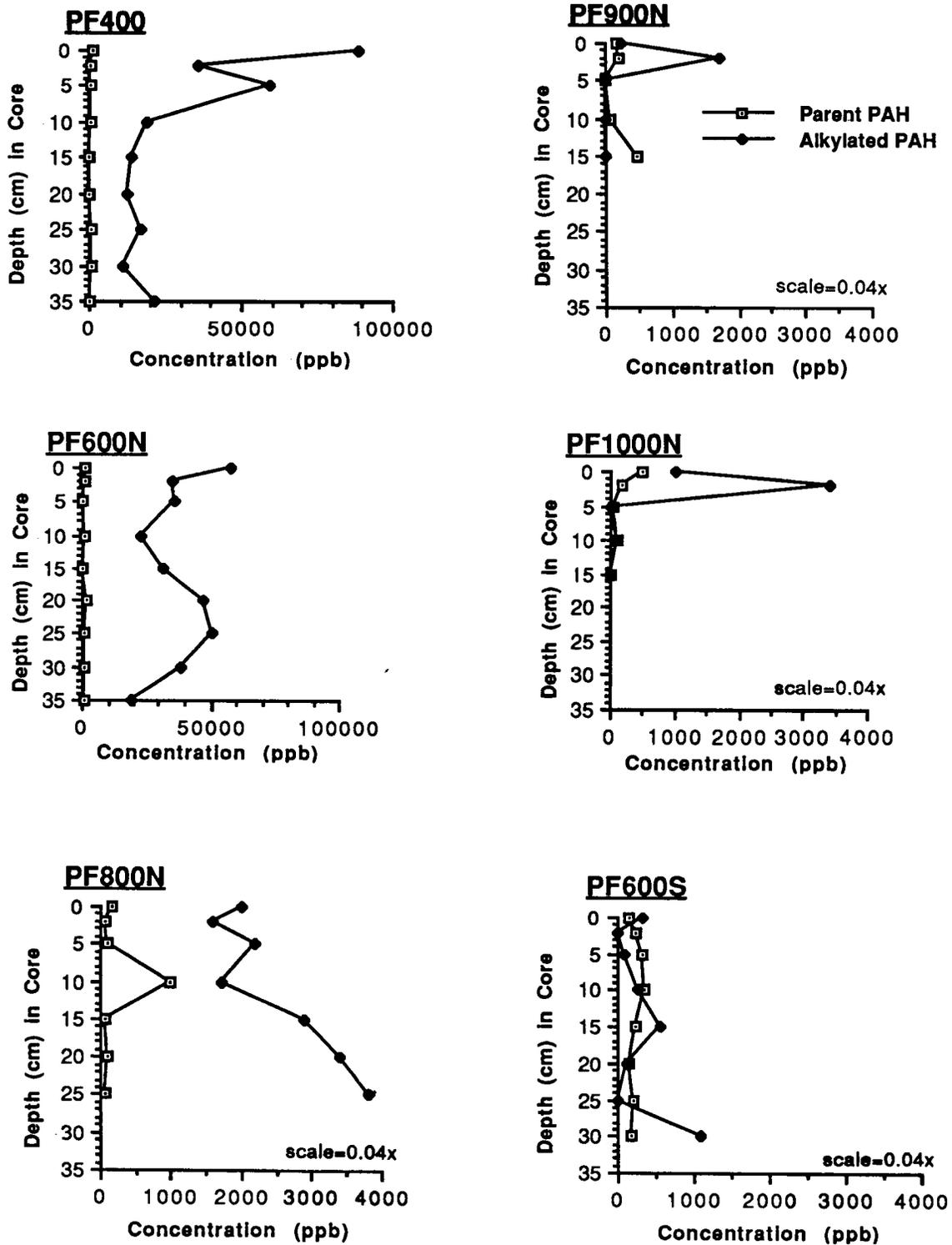


Figure 5.20. Total parent and alkylated PAH concentrations in vertical sediment core sections from Pass Fourchon, February 1990. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

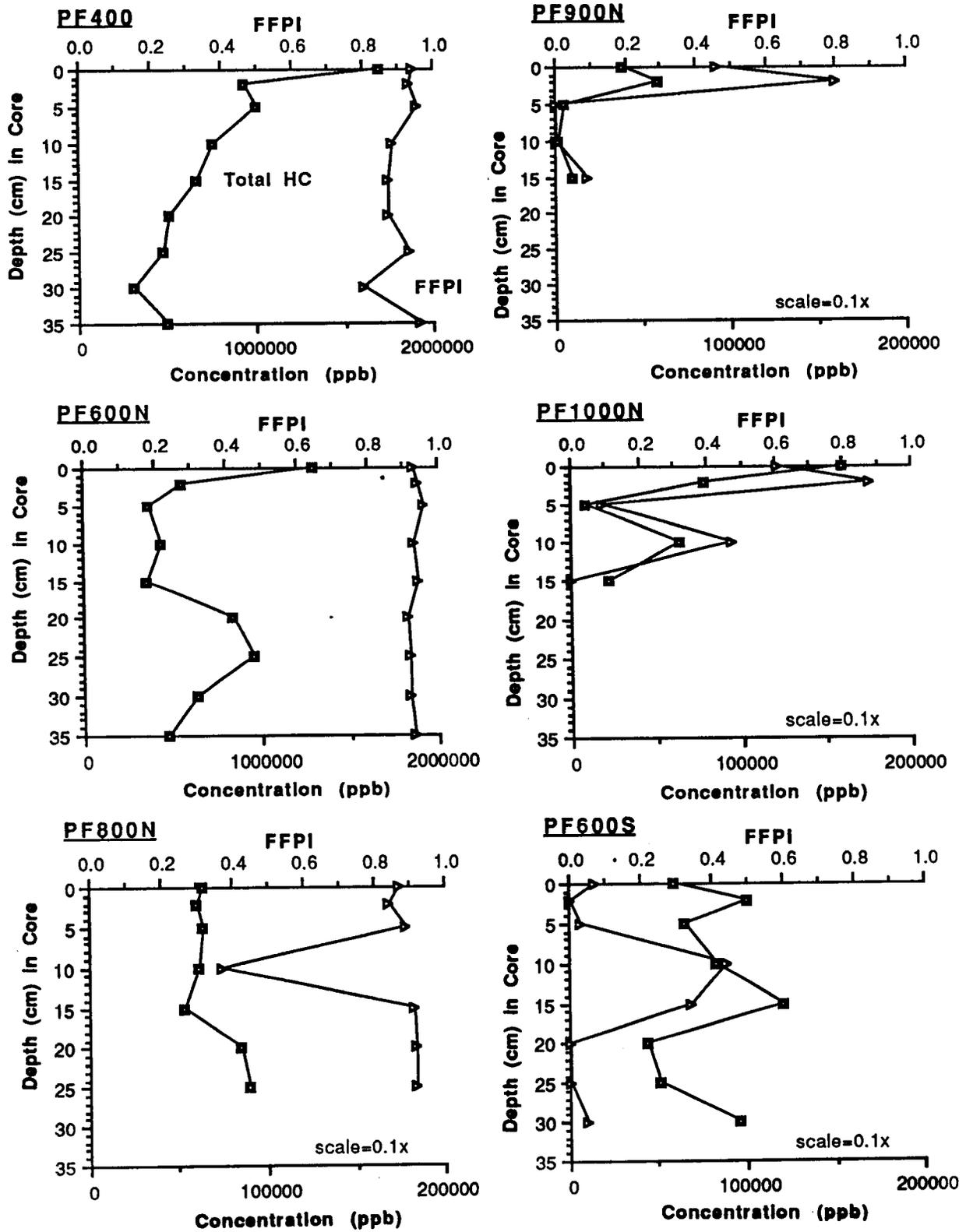


Figure 5.21. FFPI and total HC concentrations in vertical sediment core sections from Pass Fourchon, February 1990. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

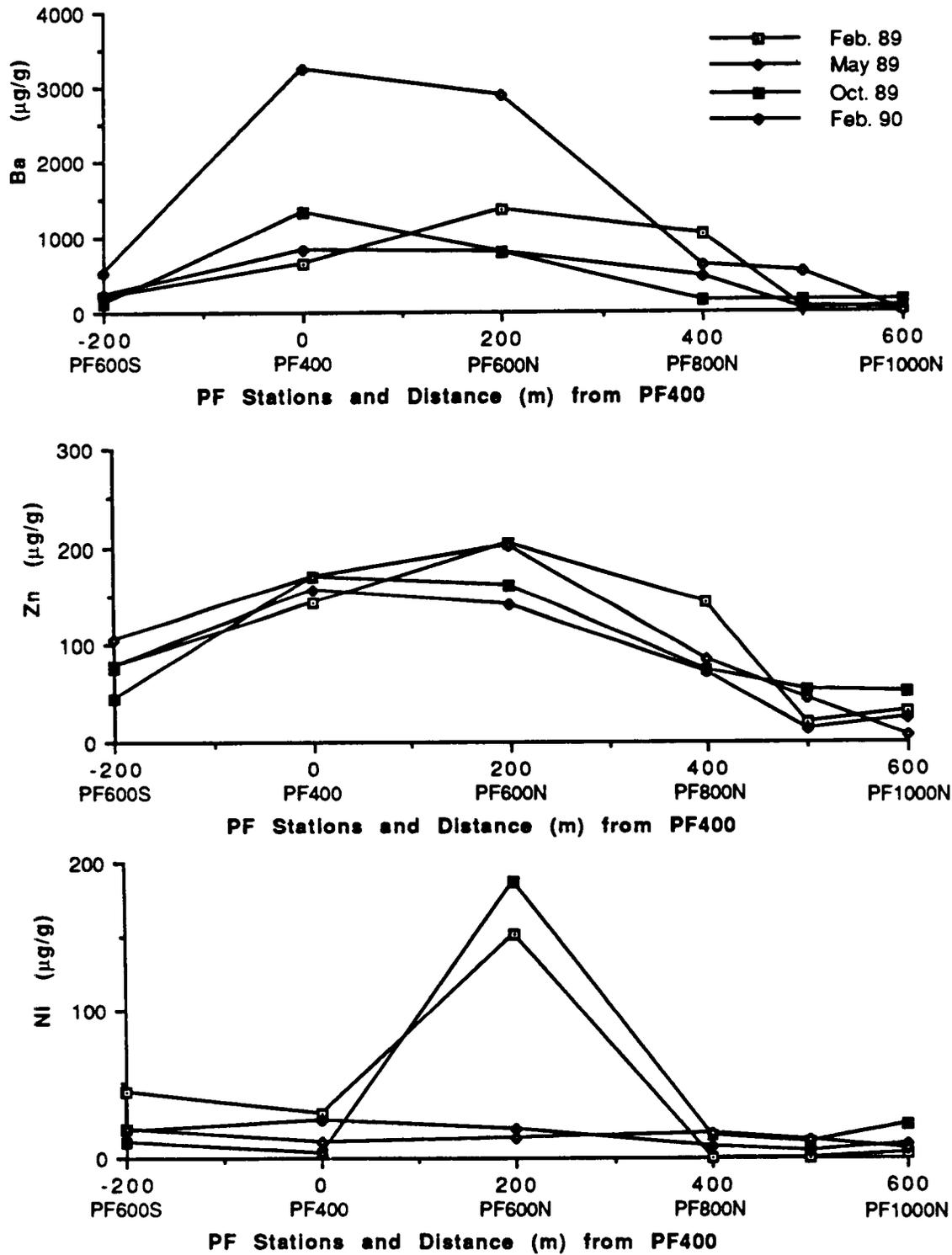


Figure 5.22. Spatial distribution of selected trace metal concentrations in surface sediments from Pass Fourchon for four sample periods.

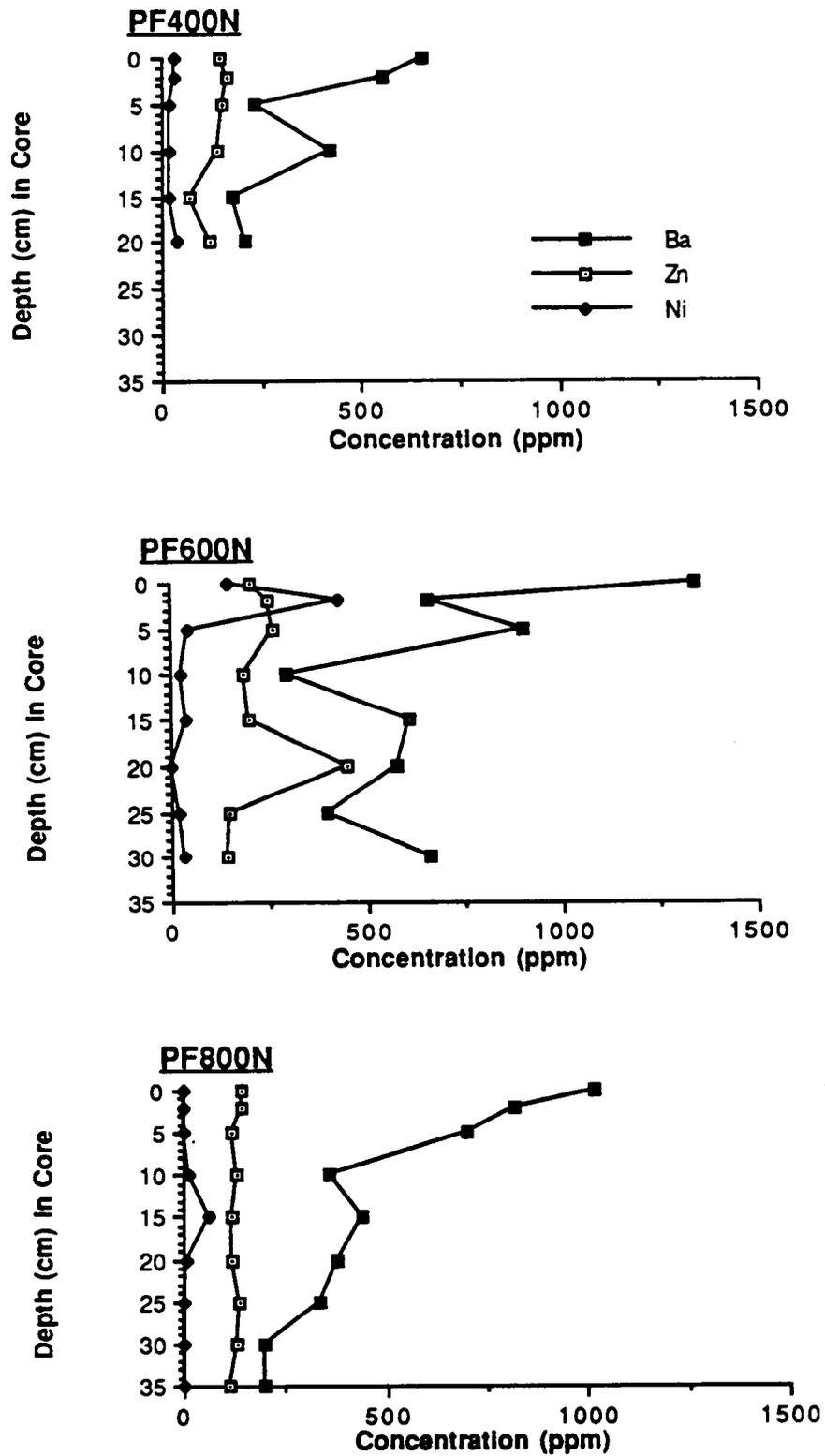


Figure 5.23. Selected trace metal concentrations in vertical sediment core sections from Pass Fourchon, February 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

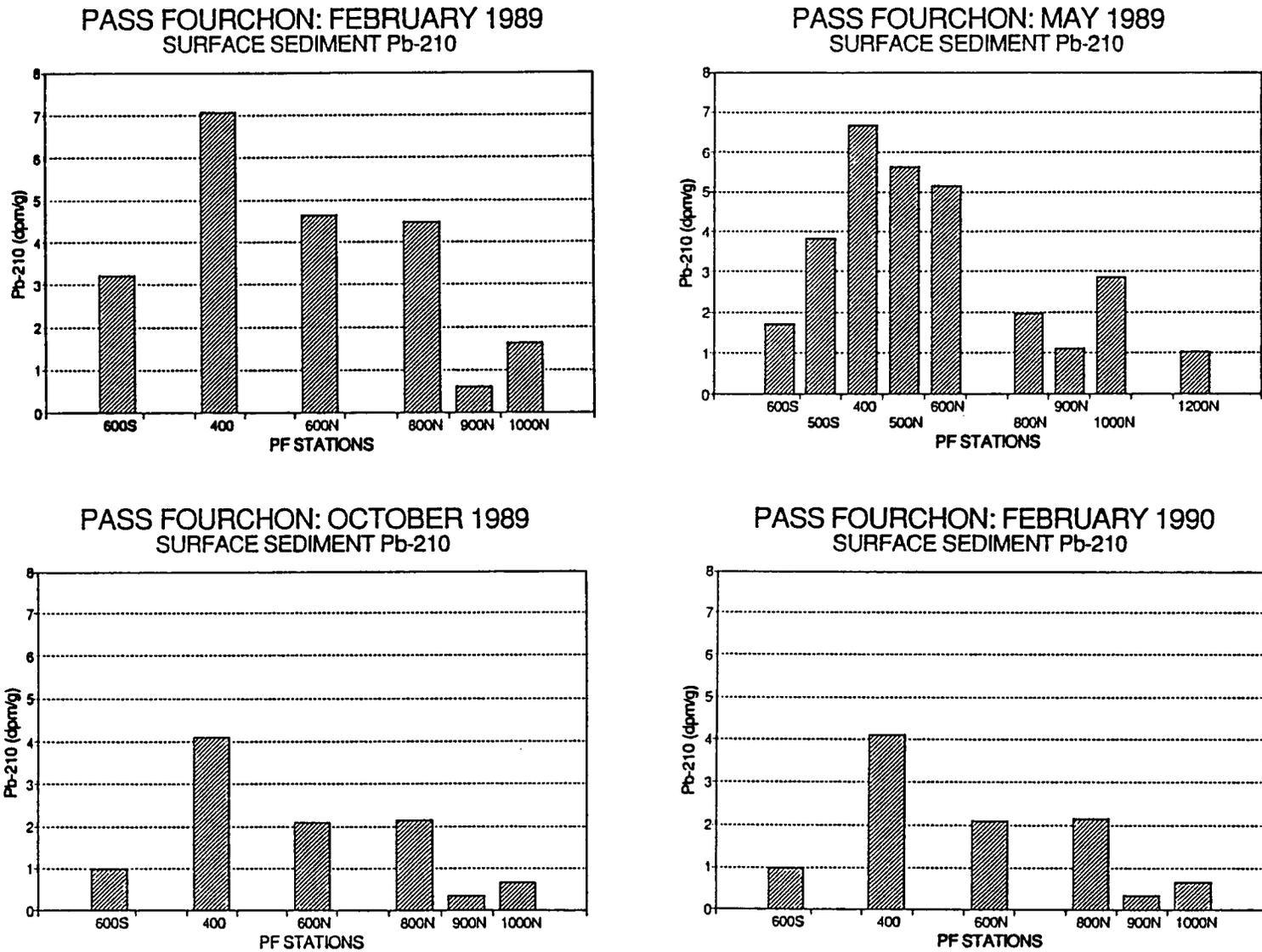


Figure 5.24. Spatial distribution of Pb-210 activities in surface sediments from Pass Fourchon for four sample periods.

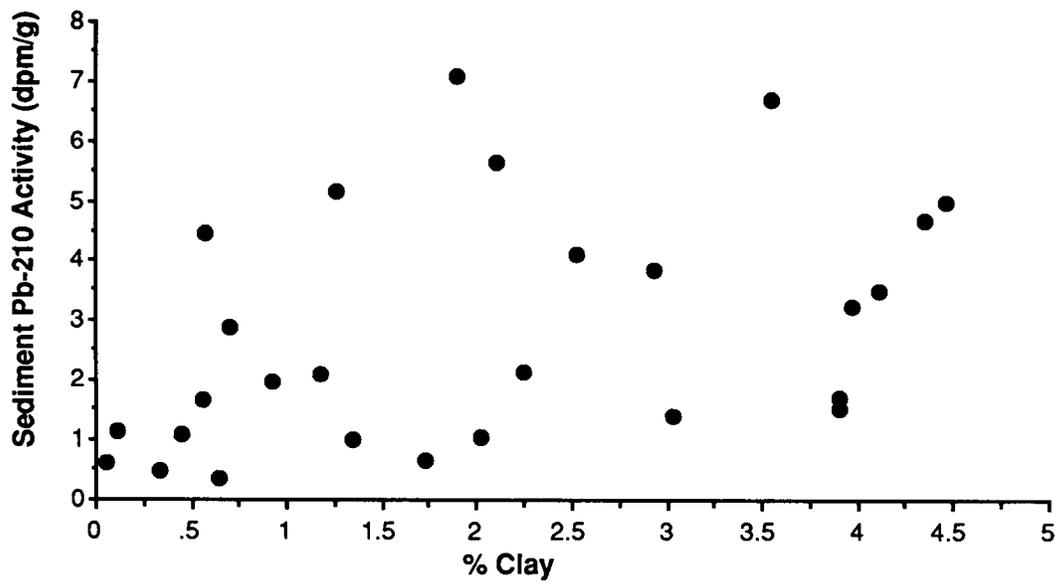
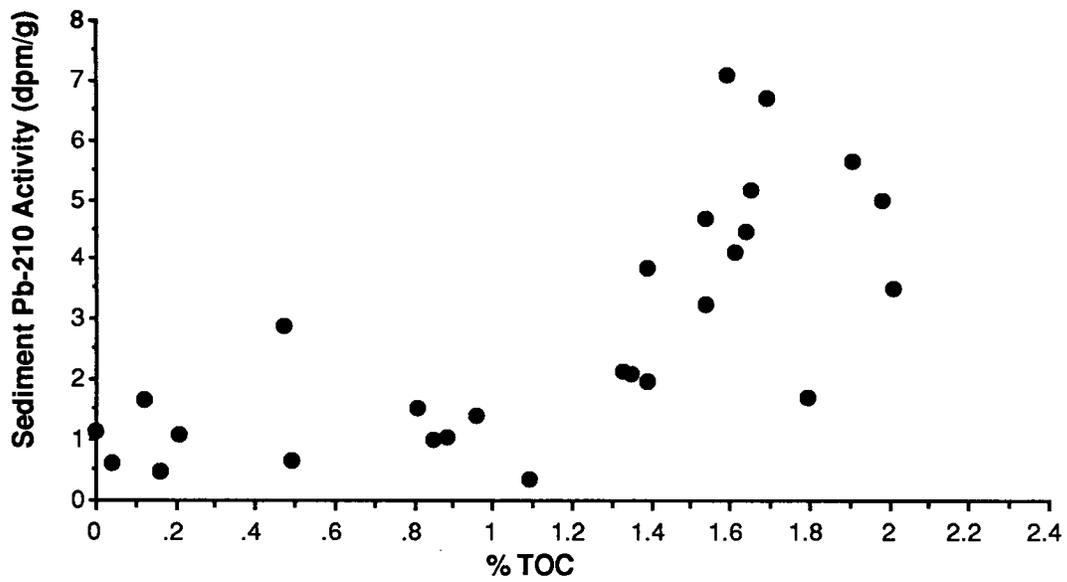


Figure 5.25. Relationship between Pb-210 activities and total organic carbon and percent clay composition of surface sediments from Pass Fourchon.

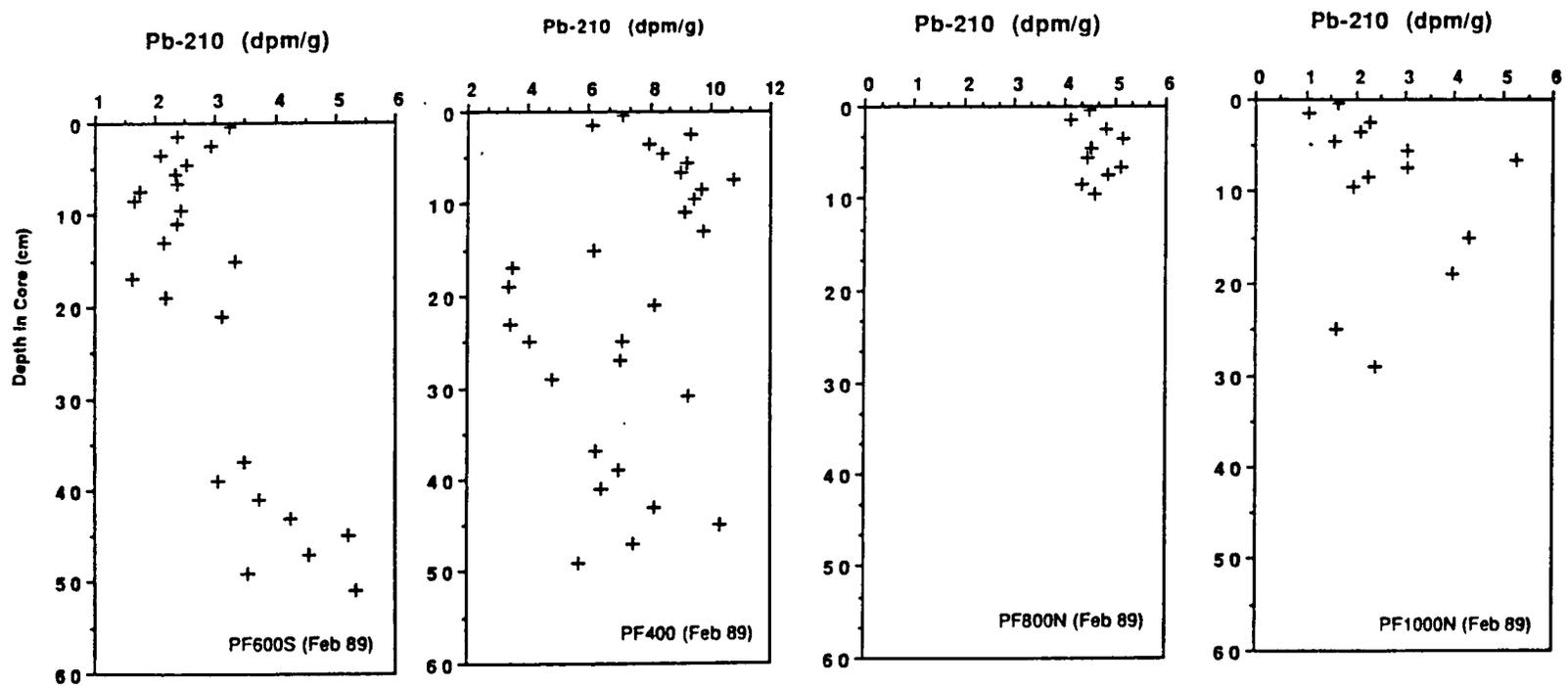


Figure 5.26. Pb-210 activities in vertical sediment core sections from selected stations in Pass Fourchon, February 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

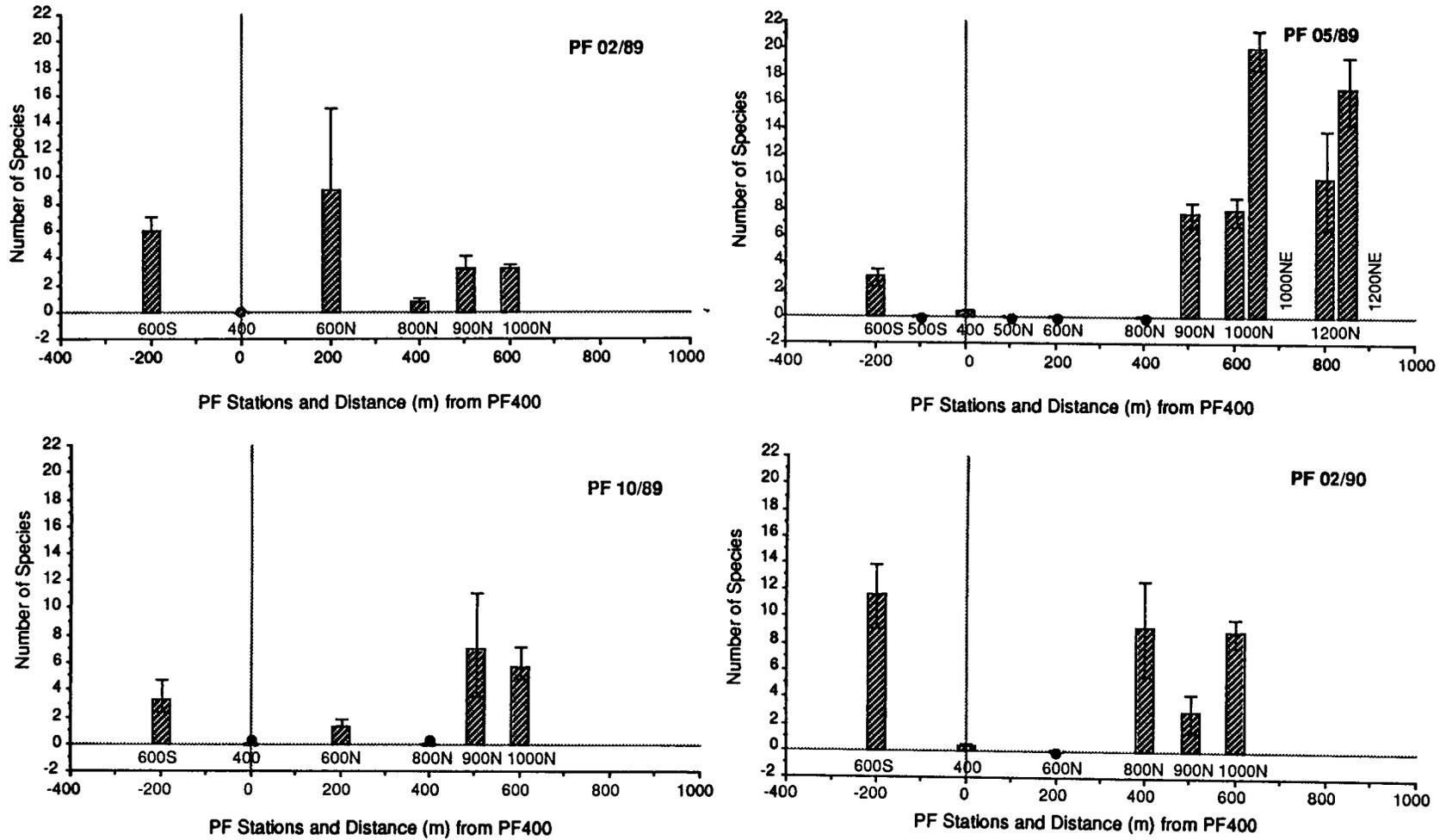


Figure 5.27. Spatial distribution of number of species per replicate (mean \pm standard error) for Pass Fourchon for four sample periods.

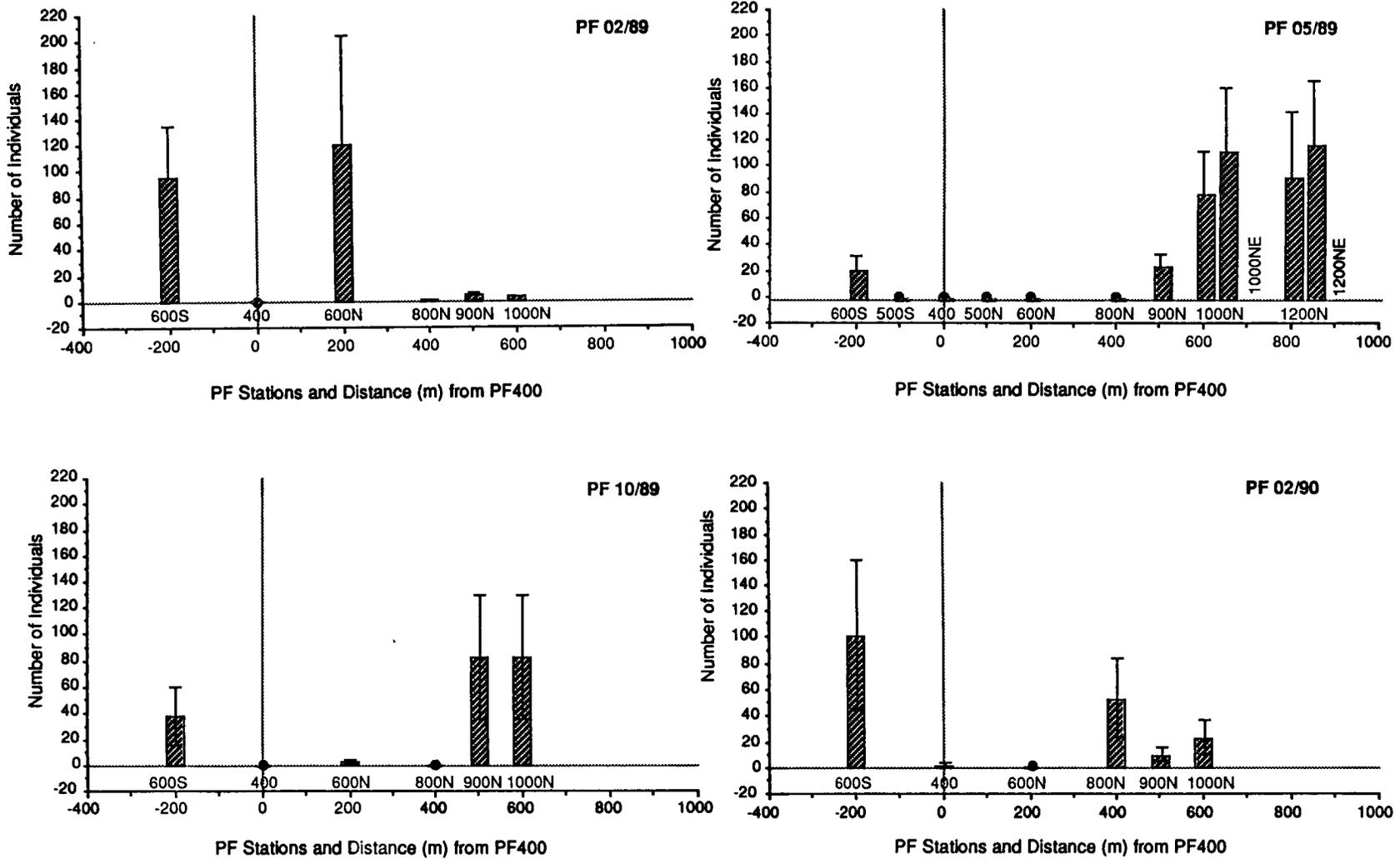


Figure 5.28. Spatial distribution of number of individuals per replicate (mean ± standard error) for Pass Fourchon for four sample periods.

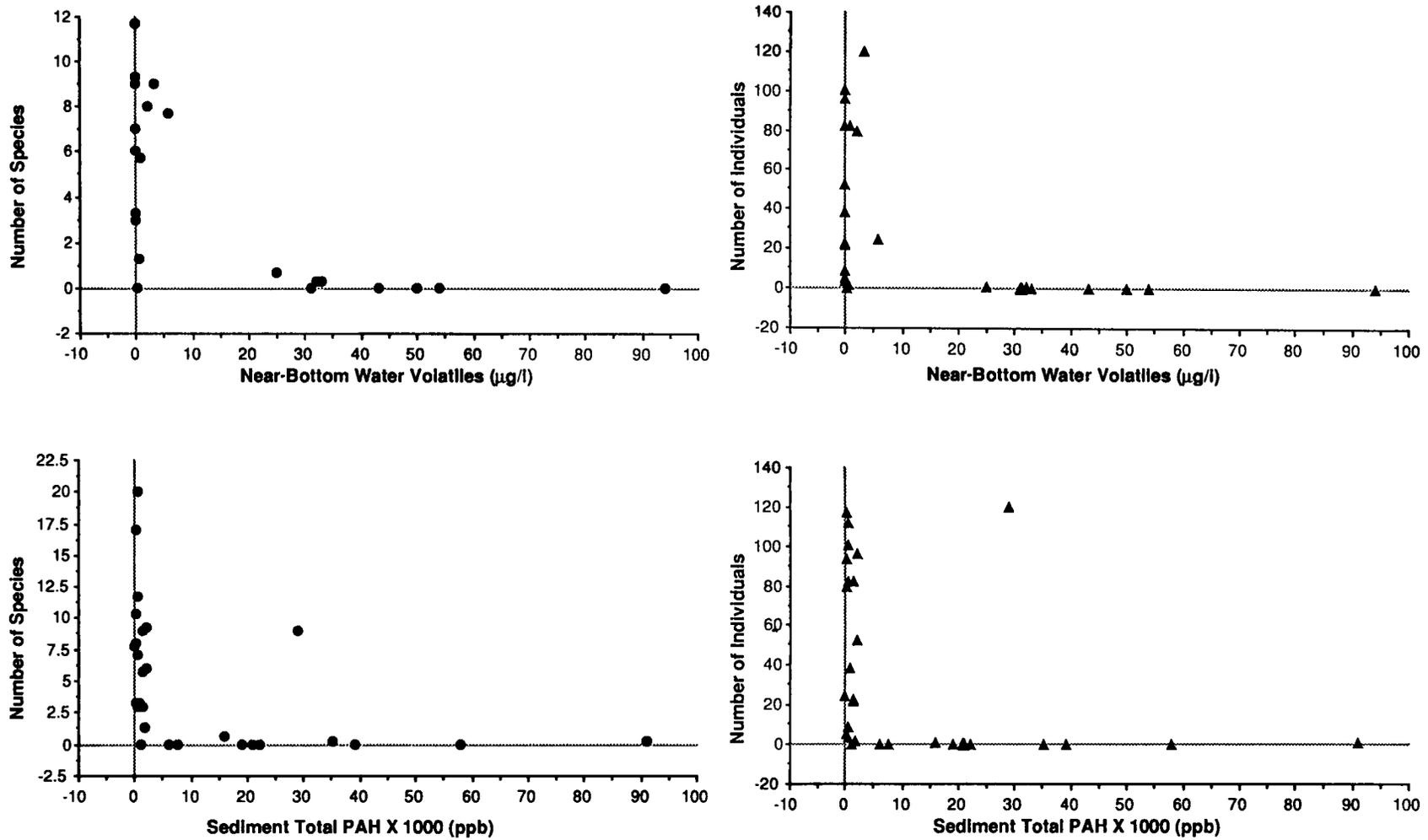


Figure 5.29. Relationship of mean number of species per replicate and mean number of individuals per replicate to near-bottom water volatile hydrocarbon concentrations and sediment total PAH concentrations for all sample periods combined at Pass Fourchon.

Table 5.1. Comparison of average daily discharges (bbl·d⁻¹) and oil and grease content (mg·l⁻¹) of produced waters from facilities at Pass Fourchon study area. (Data provided by operators.)

Date	Facility		
	PF-1 OCS	PF-2 OCS	PF-2 State
02/89			
Discharge	4,969	5,867	37,406
Oil and Grease	26	48	34
05/89			
Discharge	2,551	9,631	27,263
Oil and Grease	23	69	34
11/89			
Discharge	1,400	10,092	40,970
Oil and Grease	22	43	30
02/90			
Discharge	3,333	12,988	29,384
Oil and Grease	19	25	21
Average Discharge	4,768*	9,645**	33,756**
Average Oil and Grease	19*	40*	27*
Discharge as of 03/91	0	32,500	32,500

*Mean of 25 monthly sample dates from 02/88 - 02/90.

**Mean of 4 monthly sample dates listed.

Table 5.2. Bottom water dissolved oxygen and sulfide concentrations for Pass Fourchon study area.

Date & Station	Oxygen (mg·l ⁻¹)	Date & Station	Oxygen (mg·l ⁻¹)	Sulfide (μg-at S·l ⁻¹)
02/89		10/89		
PF200	1.08	PF200	0.40	---
PF400	1.60	PF400	2.73	tr
PF600S	7.15	PF600S	3.57	tr
PF600N	7.97	PF600N	1.78	tr
PF800N	5.56	PF800N	0.48	8.4
PF900N	8.71	PF900N	3.25	tr
PF1000N	8.62	PF1000N	3.69	tr
05/89		02/90		
PF200	1.04	PF200	0.77	---
PF500S	3.47	---	---	---
PF600S	4.47	PF600S	4.75	nd
PF400	2.12	PF400	0.09	tr
PF500N	2.54	---	---	---
PF600N	0.95	PF600N	0.29	130
PF800N	0.85	PF800N	7.36	tr
PF900N	5.40	PF900N	8.41	nd
PF1000N	5.96	PF1000N	8.42	nd
PF1000NE	6.19	---	---	---
PF1200N	6.63	---	---	---
PF1200NE	6.77	---	---	---

Table 5.3. Duncan's multiple range test for Pass Fourchon study area, February 1989; underlined stations are not significantly different from each other.

Number of Species (natural log transformed):

600N	600S	1000N	900N	800N	400
------	------	-------	------	------	-----

Number of Individuals (natural log transformed):

600S	600N	900N	1000N	800N	400
------	------	------	-------	------	-----

* Evenness (J')

1000N	900N	600N	600S
-------	------	------	------

* Stations 400 and 800N excluded from analysis due to zero values for all replicates.

Table 5.4. Duncan's multiple range test for Pass Fourchon study area, May 1989; underlined stations are not significantly different from each other.

Number of Species (natural log transformed):

1000 NE	1000 NE	1200 N	1000 N	900 N	600 S	400	800 N	600 N	500 N	500 S
------------	------------	-----------	-----------	----------	----------	-----	----------	----------	----------	----------

Number of Individuals (natural log transformed):

1200 NE	1000 NE	1200 N	1000 N	900 N	600 S	400	800 N	600 N	500 N	500 S
------------	------------	-----------	-----------	----------	----------	-----	----------	----------	----------	----------

* Diversity (H')

1000 NE	900 N	1200 NE	1000 N	1200 N	600 S	400
------------	----------	------------	-----------	-----------	----------	-----

* Cell sizes unequal due to missing values. Stations 800N, 600N, 500N and 500S excluded from analysis due to zero species for all replicates.

Table 5.5. Duncan's multiple range test for Pass Fourchon study area, October 1989; underlined stations are not significantly different from each other.

Number of Species (natural log transformed):

1000N	900N	600S	600N	400	800N
-------	------	------	------	-----	------

Number of Individuals (natural log transformed):

600S	900N	1000N	600N	400	800N
------	------	-------	------	-----	------

* Diversity (H'):

1000N	900N	600S	600N
-------	------	------	------

** Evenness (J')

1000N	600N	900N	600S
-------	------	------	------

* Cell sizes unequal due to missing values. Stations 400 and 800N excluded from analysis due to zero species for all replicates.

** Cell sizes unequal due to missing values. Stations 400 and 800N excluded from analysis due to zero values for all replicates.

Table 5.6. Duncan's multiple range test for Pass Fourchon study area, February 1990; underlined stations are not significantly different from each other.

Number of Species (natural log transformed):

600S	1000N	800N	900N	400	600N
------	-------	------	------	-----	------

Number of Individuals (natural log transformed):

600S	1000N	800N	900N	400	600N
------	-------	------	------	-----	------

* Diversity (H'):

800N	1000N	900N	600S	400
------	-------	------	------	-----

** Evenness (J'):

900N	800N	1000N	600S
------	------	-------	------

* Cell sizes unequal due to missing values. Station 600N excluded from analysis due to zero species for all replicates.

** Cell sizes unequal due to missing values. Stations 600N and 400 excluded from analysis due to zero values for all replicates.

Table 5.7. Duncan's multiple range test for Pass Fourchon study area, all sample periods combined for six stations; underlined stations or dates are not significantly different from each other.

Number of Species (natural log transformed):

1000N	600S	900N	600N	800N	400
<u>02/90</u>	<u>02/89</u>	05/89	10/89		

Number of Individuals (natural log transformed):

600S	1000N	900N	600N	800N	400
<u>02/90</u>	<u>02/89</u>	05/89	10/89		

* Diversity (H')

1000N	900N	800N	600S	600N	400

** Evenness (J')

900N	800N	1000N	600N	600S

* Cell sizes unequal due to missing values.

** Cell sizes unequal due to missing values. Station 400 excluded due to zero values in all replicates.

Table 5.8. Threshold concentrations of various chemical constituents in near-bottom waters and surficial sediments at Pass Fourchon at or above which there was a depressed benthic fauna.

Chemical Constituent	Number of Species	Number of Individuals
Near-Bottom Water:		
Volatiles ($\mu\text{g}\cdot\text{l}^{-1}$)	25	5.8
Alkylated PAH ($\mu\text{g}\cdot\text{l}^{-1}$)	0.9	0.9
Total PAH ($\mu\text{g}\cdot\text{l}^{-1}$)	1.6	1.6
Total Saturated HC ($\mu\text{g}\cdot\text{l}^{-1}$)	38	38
Surficial Sediments:		
Alkylated PAH ($\mu\text{g}\cdot\text{g}^{-1}$)	5,900	5,900
Total PAH ($\mu\text{g}\cdot\text{g}^{-1}$)	6,200	6,200
Total Saturated HC ($\mu\text{g}\cdot\text{g}^{-1}$)	250,000	50,000

Chapter 6

BAYOU RIGAUD STUDY AREA

6.1 Description of Study Area

6.1.1 General Description

Two facilities discharge large quantities of OCS-generated produced waters into Bayou Rigaud, which constitutes the industrial harbor for Grand Isle, Louisiana (Figure 6.1). Bayou Rigaud is dredged to 6 m for navigational access by offshore supply vessels. Sediments are periodically removed by dredging and likely resuspended by vessel traffic. The bayou opposite Grand Isle is shallower and grades to the contained material deposits on Fifi Island. Tidal currents through Bayou Rigaud are swift, being influenced by tidal exchange through nearby Barataria Pass on the eastern end.

The ambient salinity of the Bayou Rigaud area is strongly related to that of nearby Gulf of Mexico waters which in turn are influenced by the discharge of the Mississippi River (Geyer 1950). Salinities at the stations sampled during the study period ranged from 10 to 25 ppt. During a previous study (Boesch and Rabalais 1989a), salinities ranged between 24 and 28 ppt. The water column in Bayou Rigaud varied from well-mixed from surface to bottom to stratified with differences of 10 ppt salinity from surface to bottom. There were often east-west differences along Bayou Rigaud during a collection period.

The shoreline adjacent to the sampling stations located in Bayou Rigaud is either the dredge disposal island (Fifi Island) to the north, or bulkheaded and developed areas to the south. Additional stations located to the west of Fifi Island (May 1989) were located along more natural shoreline with some stabilization structures. The vegetation in the area to the west of Fifi Island along the northern edge of Bayou Rigaud was typical salt marsh vegetation, *Spartina alterniflora*.

6.1.2 Facilities

Conoco's Grand Isle Shore Base discharges approximately $106,000 \text{ bbl} \cdot \text{d}^{-1}$ following separation in a large separation tank and temporary storage in a large holding tank. The discharge enters the terminus of a deep slip off Bayou Rigaud into the Conoco facility. The Conoco facility began discharging produced waters in 1958. The average daily discharge for the facility was $5,000 \text{ bbl} \cdot \text{d}^{-1}$ at initiation and has grown steadily since to a discharge rate of $107,082 \text{ bbl} \cdot \text{d}^{-1}$ in February 1990 (Table 6.1). The average discharge for the facility during the period of study February 1988 - February 1990 was $105,760 \text{ bbl} \cdot \text{d}^{-1}$ and increased over the period. The hydrocarbon levels of the discharge, reported as oil and grease content, averaged $19 \text{ mg} \cdot \text{l}^{-1}$ over the same 25-month period, and the reported salinity of the discharge was 46.3 ppt chloride (83.4 ppt salinity). A series of chemicals are used to treat the water and oil product, including clarifiers, biocides and demulsifiers. During the period of the study, the brands of chemicals remained the same.

Exxon Pipeline Company acquired its Grand Isle facilities from Exxon Company USA in the early to mid 1960s. Produced water was being discharged at that time, and the facility has been in operation since. There have been no significant or long-term shutdowns since Exxon Pipeline Company acquired the facility. The average daily discharge rate for the facility was $40,000 \text{ bbl} \cdot \text{d}^{-1}$ (mean of 25 monthly averages from February 1988 - February 1990), and the rate of discharge was stable. The hydrocarbon levels of the discharge, reported as oil and grease

content, averaged $41 \text{ mg} \cdot \text{l}^{-1}$ over the same 25-month period. The reported salinity of the discharge based on samples of the effluent analyzed in September 1989 was 92 ppt.

Oil and water is received into Exxon's Grand Isle facility from offshore through a wet oil pipeline gathering system. The wet oil is first sent through a degassing and desanding tank. Low pressure gas is recovered and compressed into a vapor recovery system, which discharges to the Exxon Gas Plant at Grand Isle. The oil and water is then separated in a tank using a liquid spreader system and overflow weir. A demulsifying agent is injected into the incoming stream to ensure a quick clean break between the oil and water in the separation tank. Oil with less than 1% water is routed to a custody transfer unit for subsequent delivery to inland refineries. The separated water is pumped to a water settling tank, with a residence time of approximately one day. From this tank the water enters a baffled earthen separator system. The water travels through five weirs or baffles, then into a 50,000-barrel lagoon for final settling and separation. The surface of the weir system and the lagoon are skimmed for oil. The skimmed oil is mixed back into the incoming wet oil stream from offshore. Treated water from the 50,000-barrel lagoon is discharged to a drainage ditch which empties into Bayou Rigaud. In comparison to the Conoco Grand Isle facility, the produced water in the Exxon facility receives some aeration in the pond and traverses over a sludge bed before discharge into the drainage ditch leading to Bayou Rigaud.

6.1.3 Study Design

A series of stations were situated in Bayou Rigaud in approximately the same numbers and at approximately the same distances from the two discharges. Eleven stations were sampled on all four dates; these are BR1 through BR 11 in Figure 6.2. Of these 11 stations, six were sampled on each occasion for vertical sediment cores and are termed "secondary" stations on Figures 6.1 and 6.2. In May 1989 additional stations were added, thus intensifying the station grid near the discharges (BR1A, BR6A and BR7A) and extending the study area to the western end of Bayou Rigaud (BR12-BR16) and into the vicinity of Barataria Pass on the eastern end (BR0 and BR0A). Water depths in Bayou Rigaud averaged 4-5 m. The current meter station was located approximately 50 m northeast of station BR9. Samples were taken in February, May and October 1989 and February 1990.

Problems were encountered on several of the sampling dates in collecting benthic samples and sediments from stations BR4 and BR5 because of hard, compacted clays and shell hash, respectively. Pivoting on anchor or moving a short distance placed the research vessel over more appropriate and more easily sampled sediments.

The data for the Bayou Rigaud study area are plotted as a function of distance away from the point of the produced water discharges. Due to the existence of two discharges at the Bayou Rigaud study site, two arbitrary zero points were selected in the channel adjacent to the shoreline where the produced water effluent entered at BR9 on the western end of the study area and at BR4 on the eastern end of the study area. Data are plotted by station in Bayou Rigaud from west to east along a gradient of distance from either of the two discharge points. Transect 1 centered on the western set of stations (BR11 through BR7); transect 2 centered on the eastern set of stations (BR7 through BR1). Station BR7 was common to both transects for intercomparison, although only one set of samples was taken at this station. Station BR7 occupied the position of +350 m in transect 1 and -500 m in transect 2

6.2 Hydrography

6.2.1 Hydrographic Profiles

The water column at mid-channel in Bayou Rigaud was stratified, slightly stratified, or well-mixed on the four occasions sampled (Tables A.5 - A.8). Salinities ranged from 9 to 25 ppt

and temperatures from 14 to 27°C through the period of the study. Salinities ranged from 24 to 28 ppt during the previous study (Boesch and Rabalais 1989a).

In February 1989 the water column was slightly stratified with surface-to-bottom salinity differences of 3 ppt maximum. Water column profiles for stations adjacent to produced water discharges did not differ from those of nearby stations (Figure 6.3). There was an east-west gradient in salinity with lower salinities of 16 to 18 ppt on the western end of Bayou Rigaud and higher salinities of 21 to 23 ppt on the eastern end. Water temperatures were 18 to 19°C.

In May 1989, sampling occurred over a 2-d period. The water column was predominantly well-mixed with surface-to-bottom salinity differences seldom exceeding 1.5 ppt (Figure 6.4). Salinities ranged between 19 and 25 ppt; but there were no obvious gradients in salinity from east-to-west in Bayou Rigaud. Water temperatures were 23 to 25°C.

The water column in October 1989 (not figured) was very similar to that in May with well-mixed waters the length of Bayou Rigaud. Surface-to-bottom salinity differences seldom exceeded 0.5 ppt, and the salinity over the length of the study area ranged from 23 to 24 ppt. Water temperatures were 25 to 27°C.

The greatest differences in surface-to-bottom salinities were found in February 1990, and the water column was stratified throughout the length of Bayou Rigaud (Figure 6.5). At the most easterly station (BR1) the difference was 10 ppt, but more commonly was 5 to 7 ppt. Salinities were 10 to 12 ppt in the surface waters and 17 to 19 ppt in the bottom waters. Waters were near 15°C at all depths for most stations.

The water column was well-oxygenated from surface to bottom at all stations during all sample periods (Tables A.5 - A.8). Hydrogen sulfide was trace or not detected in near-bottom water samples (Tables A.5 - A.8). The hydrogen sulfide concentrations of the two produced water discharges into Bayou Rigaud were low; Exxon average = tr; Conoco average = 5.1 $\mu\text{g-at S}\cdot\text{l}^{-1}$.

6.2.2 Dispersion of Effluent

The salinities of the produced water discharges entering Bayou Rigaud were 100 ppt (Exxon average) and 68 ppt (Conoco average). An effluent density plume for the two produced water discharges into Bayou Rigaud was not evident from the water column CTD casts taken at mid-channel. On none of the sample dates were bottom water salinities near or adjacent to the discharges elevated above the ambient salinity, nor were gradients in decreasing salinity in bottom waters found in a direction away from the discharges.

The interstitial salinity of surficial sediments collected from box cores were not unusually elevated above the ambient levels during the period of study (Figure 6.6) nor were they indicative of elevated salinities from produced water discharges. Hydrogen sulfide levels provided no identification of produced water density plumes in the bottom waters of Bayou Rigaud.

6.2.3 Tidal Current Regime

Complete 25-hr tidal current monitoring was conducted during all four sample periods at Bayou Rigaud. The same anchor station was occupied each time. It was located approximately 50 m northeast of BR9. In order to prevent problems with supply boat traffic, the small boat was anchored at the side of the main channel in 3-4 m of water. Figure 6.7 shows the variation in mean velocity during the February 1989 sample period. Flood velocities were to the southwest at this location, from Baratavia Pass into Bayou Rigaud. Ebb velocities were to the northeast.

An asymmetry between flood and ebb was apparent with mean velocities on the flood only reaching $0.32 \text{ m}\cdot\text{s}^{-1}$, while on the ebb mean velocity reached over $0.5 \text{ m}\cdot\text{s}^{-1}$. The predicted range of this tide was 1.5 ft. Similar asymmetry was apparent in May 1989 (Figure 6.7) on a 1.3 ft predicted tide, although the velocity difference between the flood and ebb maxima was only $0.06 \text{ m}\cdot\text{s}^{-1}$. The same pattern was repeated in October 1989 on a 1.5 ft predicted tide (Figure 6.8) and in February 1990 on a 1.4 ft predicted tide (Figure 6.8). In coastal Louisiana, meteorological conditions frequently influence tidal currents and consequently the predicted tidal range provides only an estimate of the potential magnitude of the tidal flux.

6.2.4 Velocity Profiles

The velocity profiles obtained during sampling at Bayou Rigaud allowed the calculation of shear velocities (U_*) from the slope of the logarithmic profile. The asymmetry shown in the mean velocity variations for each sample period was not as clear in similar plots of U_* . In February 1989 (Figure 6.7) the maximum shear velocities occurred on the ebb tide. The magnitude of the shear velocities was almost an order of magnitude greater than at Pass Fourchon stations, and, as bed shear stress is proportional to shear velocity, there is greater potential for sediment entrainment and transport close to the bed. Although the asymmetry for the mean velocity showed ebb domination for all sample periods, the plots of shear velocity showed greater variation. In May 1989 (Figure 6.7) the highest shear velocities were reached during flood tide, while in October 1989 (Figure 6.8) there was no pronounced difference between flood and ebb tides. Again in February 1990 (Figure 6.8) the highest shear velocities were reached during the flood tide. These data show that sediment entrainment from the bed during either flood or ebb tides is possible. Dyer (1986), in his summary of theoretical threshold velocities for sediment movement, indicates that at shear velocity values of greater than $0.01 \text{ m}\cdot\text{s}^{-1}$, grains of 0.1 mm in diameter will be entrained. Clearly, threshold velocities vary with grain size and are influenced by local bed conditions. However, the magnitude of shear velocities reported from Bayou Rigaud indicates that sediment entrainment is possible on both ebb and flood tides.

6.3 Water Column Contaminants

6.3.1 Hydrocarbons

The near-bottom water data for Bayou Rigaud are presented in Figure 6.9 and Tables D.5 - D.8. The volatile hydrocarbons detected in Bayou Rigaud were dwarfed by the sample from BR4 (at the Conoco discharge) during February 1989 ($110 \mu\text{g}\cdot\text{l}^{-1}$). At no other time in this study area did total volatiles approach 10% of this value. This value seemed to be the exception, since volatiles in Bayou Rigaud typically were $<10 \mu\text{g}\cdot\text{l}^{-1}$. The PAH data was also dominated by one sample, BR8 during October 1989 ($22 \mu\text{g}\cdot\text{l}^{-1}$), which was ten times higher than any other sample. PAH were not normally detected in Bayou Rigaud near-bottom waters. During February 1989 the highest concentrations of volatile hydrocarbons and PAH in near-bottom waters were opposite a discharge (BR4); otherwise, both the volatile and PAH data were highly variable with a different station showing the most contamination at each sampling. The variability in these data was the result of the swift currents and boat traffic present in Bayou Rigaud, which help mix the discharge waters with the surrounding water. These factors also affected the ability to get a representative sample of water near the bottom.

6.3.2 Radionuclides

Pb-210: During February 1989, Pb-210 activities in near-bottom waters were highest at station BR4 (closest to the Conoco discharge) with an activity of $2.96 \text{ dpm}\cdot\text{l}^{-1}$, about 30 times greater than natural levels (Figure 6.10, Table F.2). Pb-210 activities in near-bottom waters elsewhere in the study area were all within the range of natural water Pb-210 activities.

During May 1989, Pb-210 activities ranged from 0.09 to 1.02 dpm·l⁻¹, up to 10 times greater than natural levels (Figure 6.10, Table F.2). No general spatial trend was apparent. These Pb-210 activities were lower than observed in February 1989, perhaps reflecting the lower Pb-210 activities of produced waters during this time period.

During October 1989, Pb-210 activities ranged from 0.07 to 0.71 dpm·l⁻¹, exhibiting no apparent spatial trend (Figure 6.10, Table F.2). Pb-210 activities were highest at BR11 where they were about 7 times higher than natural levels. Most of the samples collected had natural levels of Pb-210.

During February 1990, Pb-210 activities ranged from 0.01 to 0.28 dpm·l⁻¹ (Figure 6.10, Table F.2). All stations, except BR4 and BR6 had Pb-210 activities that were within the range of natural levels. At BR4 and BR6, Pb-210 activities were about 2 times higher than natural waters.

Radium: In all water samples, U-238 and Th-234 activities were below detection levels (<0.5 and <0.8 dpm·l⁻¹, respectively). This lack of enhanced uranium and thorium activity indicates strongly that the high radioactivity levels associated with produced waters originate with the radium isotopes and is not supported by radioactive parents of radium which are higher in the decay chain. Total radium is the sum of Ra-226 and Ra-228 activities. The ratio of Ra-226/total Ra varies from site to site for produced waters, but in most cases the Ra-226 activity constitutes more than two-thirds of the total radium activity.

During February 1989, total radium activities in near-bottom waters were highest at BR2 (close to the Conoco discharge) with an activity of 59 dpm·l⁻¹, about 30 times greater than natural levels (Figure 6.11, Table F.2). Total radium activities elsewhere in the study area ranged from 17 to 46 dpm·l⁻¹, 9 to 23 times greater than natural water radium activities.

During May 1989, total radium activities ranged from 31 to 71 dpm·l⁻¹, up to 35 times greater than natural levels (Figure 6.11, Table F.2). No general spatial trend was apparent, but activities generally followed salinity values.

During October 1989, total radium activities ranged from 29 to 81 dpm·l⁻¹, exhibiting no apparent spatial trend (Figure 6.11, Table F.2). Radium activities were highest at BR4 where they were over 40 times higher than natural levels.

During February 1990, total radium activities ranged from 29 to 75 dpm·l⁻¹, 15 to 38 times higher than natural waters (Figure 6.11, Table F.2).

6.4 Sedimentary Characteristics

6.4.1 Grain Size Distribution

During sampling in February (Figure 6.12) and May 1989 (Figure 6.13), grain size distributions of surface sediments at all stations were characterized as muddy sand (Table B.1). Samples were typically >70% sand and <3% clay. Silt content was greatest at BR3, BR4 and BR10 in February 1989, and BR2 and BR6A in May 1989. There was no consistent spatial pattern in the variation of silt and clay content. In October 1989 sand content decreased markedly to 50% or less (Figure 6.14), with the exception of BR2 (52% sand). Surface sediments in October can be characterized as sandy muds. Again there was no clear spatial pattern to the variations in grain size distribution. In February 1990, sand content of all samples again decreased and was 20% or less at all stations except BR2 (21%) (Figures 6.15). Clay content increased to as much as 10% (BR7). Although there was no apparent spatial pattern, the decreasing sand content found in BR samples during October 1989 and February 1990,

compared to February and May 1989, was similar to the temporal changes identified at Port Fourchon for the same sample periods.

6.4.2 Total Organic Carbon (TOC)

TOC content of surface sediments in Bayou Rigaud varied between 0.6% and 2.6% (Table B.1). There was no clear spatial pattern for each sample period, and there was also some variation between sample periods for the same stations. In February 1989 TOC values were highest at BR4 and BR9 (both >2%) and lowest at BR1 (0.9%) (Figure 6.16). During the more intensive sampling in May 1989, nine of the 21 stations showed TOC values greater than 2% (Figure 6.17). All other stations ranged between 1% and 2% with the exception of BR3 (0.6%) which had the lowest value found at any Bayou Rigaud station during the entire study. Values were generally lower in October 1989 (Figure 6.18) with only one station, BR8 over 2%. The lowest value for this sampling period was 0.8% at BR2. There was no clear pattern to the variation between stations. During the final sampling in February 1990, the pattern of variation was again different from previous periods. The highest TOC content was at BR9 (2.6%) and the lowest was 0.7% at BR7 (Figure 6.19). Overall there was considerable variation in TOC content both between stations and between sample periods, but no clear pattern to this variation was apparent.

6.5 Sediment Contaminants

6.5.1 Hydrocarbons

6.5.1.1 Surficial Sediments

The concentrations of normal petroleum hydrocarbons, as well as petrogenic alkylated aromatic hydrocarbons (alkylated PAH), related pyrogenic aromatic hydrocarbons (parent PAH) and Fossil Fuel Pollution Index (FFPI) are shown in Figures 6.20 - 6.27 and detailed in Tables D.20 - D.24.

Figure 6.21 shows the spatial distribution of alkylated PAH along transect 2 during February 1989. Maximum alkylated PAH concentrations (~40,000 ppb) were observed at BR3 and declined in both the east and west directions away from the Conoco discharge. Parent PAH concentrations were very low relative to the alkylated PAH concentrations at all stations with the exception of BR1 500 m to the east of the discharge. This conclusion is supported by the fact that the values of FFPI calculated for these samples were consistently high, except for BR1 where the value dropped to a value <0.5, indicating pyrogenic sources of PAH. A slight decline in FFPI values was also observed to the west toward BR7 (FFPI~0.65). It should be noted that these values increased again to values >0.8 at all of the stations further to the west along transect 1 (Figure 6.20). Alkylated PAH concentrations also increased to the west along transect 1 up to a secondary maximum of ~7,000 ppb near the Exxon discharge (BR9) and then declined further to the west. It is interesting to note that while a decrease in alkylated PAH concentrations was observed at BR10 and BR11, no decrease in FFPI values was observed as was seen at BR1.

Aliphatic hydrocarbon concentrations in Bayou Rigaud sediments followed a pattern very similar to that of the alkylated PAH along transect 2, but a general decline in total hydrocarbons was observed along transect 1. The maximal concentration observed along transect 1 was at the linking station (BR7). Thus, it appeared that far less of the aliphatic hydrocarbon fraction was being discharged from the Exxon site.

In somewhat of a contrast to February 1989, in May 1989 the alkylated PAH concentrations were substantially lower at stations within 400 m of BR4 nearest the Conoco discharge (Figure 6.23). They ranged from 1,500 to 4,300 ppb while in February 1989 they

ranged from 4,000 to 40,000 ppb. The sharp decline of alkylated PAH at and beyond BR1 to the east was similar to that observed in February except that FFPI values at these stations were now <0.05 indicating that pyrogenic PAH dominated the aromatic fraction at BR0, BR0A and BR1. A decline in alkylated PAH with a decrease in FFPI values was also seen to the west at BR6A and BR7 (Figure 6.22). Alkylated PAH concentrations along transect 1 were highly variable, exhibiting several secondary maxima toward the west. While this variable pattern was observed, the concentrations of alkylated PAH at those stations occupied previously were more similar (within a factor of 2) than those changes observed to the east (more than an order of magnitude). Large shifts were also observed in FFPI values along transect 1. Maxima in FFPI were generally associated with maxima in alkylated PAH concentrations in the sediments suggesting that import of relatively contaminated sediments had occurred at some of these sites.

Aliphatic hydrocarbon concentrations showed a similar decrease at BR3 and a more diffuse distribution along transect 2, with concentrations ranging between 100,000 and 160,000 ppb. Interestingly, the concentration of total hydrocarbons at BR4 nearest the Conoco discharge decreased from $\sim 200,000$ ppb to $\sim 75,000$ ppb between February and May. Aliphatic hydrocarbon concentrations at BR0 and BR0A continued to decrease to very low levels. Aliphatic hydrocarbon concentrations in sediments collected along transect 1 were variable like the alkylated PAH data and, although there was a general decrease with distance toward the west, some secondary maxima were observed at stations BR10 and BR14 (150 m and 850 m, respectively to the west of the Exxon discharge point).

In October 1989 the distribution of alkylated PAH concentrations had a maximum at BR4 of $\sim 17,000$ ppb, with decreasing concentrations observed at stations to the east and west along transect 2 (Figure 6.25). This maximum concentration was an increase from May 1989 and was similar to that originally seen in February. A maximum FFPI value was also observed at BR4, with values of this parameter decreasing to ~ 0.7 at both ends of the transect. These data seem to suggest that alkylated hydrocarbon concentrations were building up at the stations closest to the Conoco discharge after the large decrease which occurred between February and May of 1989. Alkylated PAH concentrations along transect 1 (Figure 6.24) were somewhat variable at BR7 through BR10, ranging from $\sim 2,700$ ppb to $\sim 4,500$ ppb, but then declined to much lower values at BR11 further to the west. A similar pattern of FFPI values was observed at these same stations with values ranging from ~ 0.5 to 0.75 between BR7 and BR10, while at BR11 the value dropped to <0.05 .

Aliphatic hydrocarbon concentrations in October 1989 cores showed a maximum value of $\sim 400,000$ ppb at BR4. Total HC concentrations declined in both directions along transect 2 (Figure 6.25). As was observed with the alkylated PAH, total HC concentrations increased substantially from May to October in the stations nearest the Conoco discharge but were still less than was observed in February 1989. This tends to support the hypothesis that produced water associated hydrocarbons were building up rapidly in the sediments nearest the Conoco discharge after the decrease that occurred before the May sampling. Total HC concentrations in sediments along transect 1 showed a general decline toward the west, returning to a distribution pattern more similar to that originally seen in February 1989 (Figure 6.24).

Data for February 1990 (Figures 6.26 and 6.27) indicated that alkylated PAH distributions were similar to the previous February with a maximum observed again at BR3 just to the east of the Conoco discharge and decreasing levels seen in sediments both to the east and west along transect 2. FFPI values along this transect increased to values >0.8 for all stations, except BR1 farthest to the east which was ~ 0.5 . Alkylated PAH concentrations along transect 1 were very similar to the preceding February showing a maximum at BR9 nearest the Exxon discharge and decreasing to the west. FFPI values were 0.8 or greater near the discharge but declined to ~ 0.55 at BR11. This was not seen in the previous year.

Aliphatic hydrocarbon concentrations along transect 2 were similar to those of the alkylated PAH in February 1990, except that a secondary maximum was observed at BR6 which was similar to the concentrations observed near the Conoco discharge at BR3. Lower values were observed at the intermediate stations BR4 and BR5. Total hydrocarbon concentrations along transect 1 were similar to those observed in the preceding February and paralleled the pattern of the alkylated PAH in the region.

The temporal changes along transect 1 were relatively small for both the alkylated PAH and total HC; however, large shifts in alkylated PAH and total HC were seen along transect 2. Figure 6.28 shows the temporal changes which occurred during the year at three stations in the eastern portion of Bayou Rigaud which bracketed the Conoco discharge. Alkylated PAH concentrations at station BR3 just to the east of the discharge canal decreased by an order of magnitude between February and May of 1989. As discussed earlier, changes in the FFPI values, as well as the dramatic shift in concentrations at this station suggest a large disruption of the sediment bed such as dredging or a major storm event. According to the Louisiana Monthly Weather Review, February and March of 1989 were stormier at New Orleans than the 20-yr average. Several strong weather systems moved through the area. Following the decrease in May, alkylated PAH concentrations continued to increase to a level equal to approximately three-fourths of the original concentrations. At stations BR4 and BR5, less dramatic decreases were observed, followed by an increase in October 1989 and a decrease in February 1990. These variations seemed consistent with some disruption of the sediments followed by a period of accumulation, followed by additional disruptions of the sediment bed. Trouble in positioning of the research vessel at stations BR4 and BR5 may have also accounted for some of the variability.

The total HC concentrations in the sediments at the same three stations followed a similar pattern to that observed with the alkylated PAH, except that total HC levels remained relatively constant at station BR5 through the study period. At BR3 the same large decrease was observed between February and May of 1989, followed by a steady increase. Levels in February 1990 were approximately 60% of the levels one year earlier. At BR4 total HC levels decreased, followed by an increase and then decreased just as alkylated PAH concentrations had.

These data suggest that the Bayou Rigaud system is impacted over a distance of approximately one kilometer with the eastern portions of the estuary being more heavily impacted than the western portions. The reasons for this may be the larger volume and hydrocarbon loading of the Conoco discharge relative to the Exxon discharge or it may be the result of the accumulated effects of both discharges building as sediments are transported to the east and the mouth of the estuary. Ebb currents were stronger on the four dates sampled, and may be expected to transport sediment to the east.

6.5.1.2 Vertical Profiles

6.5.1.2.1 February 1989

Figures 6.29 and 6.30 show the hydrocarbon depth profiles for sediment cores taken in Bayou Rigaud, February 1989. Complete data is presented in Tables D.44 - D.49. In general, cores from this sampling showed highest concentrations of total HC at the surface, 0-5 cm, and bottom sections of the core, with reduced levels somewhere in the central portions, generally at 15-20 cm. The BR11 core was the exception. This trend was not as clear for alkylated PAH. Most stations showed maximal PAH concentrations near the bottom of the core, exceptions were BR2 and BR6.

BR2: Highest concentrations of alkylated PAH and total HC in the BR2 core were at the surface and in the 20-25 cm section. The highest values were 5,800 ppb alkylated PAH and 160,000 ppb total HC in the surface section. The lowest values for alkylated PAH were found in

the 5-20 cm sections, about 1,200 ppb. Total HC were lowest in the 5-15 cm sections, averaging 37,000 ppb. Average concentrations were 3,200 ppb alkylated PAH and 93,000 ppb total HC. FFPI values followed the pattern of concentrations with the exception of a rise in value at 30-35 cm, where concentrations were stable. Average FFPI was 0.75 and ranged from 0.60 at 25-30 cm to 0.89 at the surface. The ratio R/T averaged 0.09, indicating a high degree of weathering, and was somewhat higher in the surface section. The percent composition of total PAH due to naphthalenes followed the same pattern as total PAH concentration, dropping to only trace values in the 15-20 cm section and showing typical composition, 50-60%, where concentrations were maximal. The phenanthrenes followed an inverse pattern, showing highest contribution to total PAH, 59%, in the 15-20 cm section. Fluorenes and dibenzothiophenes averaged 10% each of total PAH and showed minimal variation from this value when detected.

BR4: The profile for this core showed a slight increase in alkylated PAH and total HC concentrations just below the surface at 2-5 cm and a general increase to a maximum at 30-35 cm for alkylated PAH and 35-41 cm for total HC. Alkylated PAH values ranged from 9,400 to 42,000 ppb, while total HC ranged from 160,000 to 840,000 ppb, the highest levels for all vertical cores sampled in February 1989. FFPI remained high throughout, averaging 0.93, indicating a high percentage of petrogenic inputs. R/T values ranged from 0.15 to 0.33 and averaged 0.23, higher than for other stations, indicating less weathering of petrogenic hydrocarbons than observed at other stations. Naphthalenes comprised an average of 74% of the total PAH, the highest average found in this study area, a reflection of fresh inputs of petroleum hydrocarbons.

BR6: A subsurface (2-5 cm) elevation in both alkylated PAH and total HC seen in the BR6 core was similar to BR4. Alkylated PAH concentrations remained constant in the deeper sections and averaged 3,500 ppb throughout, similar to levels found in BR2. Total HC concentrations were not uniform, but generally increased with depth to a level equal with that at 2-5 cm, 190,000 ppb. Average total HC concentrations were similar to BR2. FFPI values decreased to a low of 0.39 at 15-20 cm, corresponding with a low concentration of both alkylated PAH and total HC and maximal pyrogenic PAH. This suggested a time period where petrogenic inputs were low or absent, while pyrogenic deposits or accumulation increased slightly. R/T values were generally low, averaging 0.11, indicating a high degree of weathering. The naphthalenes composition averaged 54% of total PAH, but was higher, 65-70%, in the 5-10 cm, 10-15 cm, and 25-30 cm sections, a trend that did not correspond to trends in either PAH or total HC concentrations.

BR8: Data for alkylated PAH showed a variable pattern with a general increase with depth. Total HC concentrations and FFPI values both showed a decrease toward the middle of the core, 15-20 cm, and all values were highest at the bottom of the core, typical of cores from this period. In addition, parent PAH concentrations rose slightly in the 15-20 cm section, similar to BR6. Average concentrations of alkylated PAH and total HC were 5,500 and 130,000 ppb, respectively, an increase from BR6. R/T values remained low, averaging 0.13. Naphthalenes were predominant in all sections but were highest, 74% of total PAH, in the bottom 35-38 cm section and lowest in the central sections, 35% in the 15-20 cm section, reflecting the rise in parent PAH and following the decrease in total HC concentration.

BR9: The depth profile for this station was very similar to the pattern shown in the BR4 core. Concentrations of alkylated PAH and total HC were somewhat higher than in BR8, but not as high as BR4, as might be expected due to the proximity of the station to the Exxon discharge site. Average concentrations were 8,700 ppb alkylated PAH and 170,000 ppb total HC. FFPI values were high until the bottom section, averaging 0.85. At this station, FFPI values did not drop in the middle of the core where concentrations of alkylated PAH and total HC fell. R/T values averaged 0.14, similar to other stations not directly adjacent to a discharge site. Naphthalenes composition averaged 53% of total PAH, showing minimal variation between

sections. Phenanthrenes averaged 19% of total PAH and decreased from 27% at 2-5 cm to 10% in the 30-37 cm section, which corresponded to a drop in the FFPI and total HC concentrations, but not to the trend for alkylated PAH. This is explained by an unusually high concentration of almost all targeted parent PAH, with several at concentrations greater than 1,000 ppb in the 30-37 cm section only.

BR11: The pattern for this core showed a general increase in petrogenic substances with depth, with a slight decrease just below the surface. Concentrations averaged 2,700 ppb alkylated PAH and 78,000 ppb total HC, lower than BR9 and similar to BR6. FFPI values were erratic throughout, ranging from 0.60 to 0.88, averaging 0.74. There was no clear reason for the variable pattern of FFPI. Naphthalenes generally increased in composition of total PAH, from 37% at the surface to 71% in the 30-36 cm section. Phenanthrenes generally decreased with depth, from 27% at the surface to 10% of total PAH in the bottom section. Parent PAH did not show any consistent trend; different PAH were singularly high in separate sections of the core. Phenanthrene, fluoranthene, pyrene, and chrysene were detected in every section and maximized near the bottom sections, but not simultaneously. R/T values remained low throughout the core, averaging 0.10, similar to other stations removed from the discharge area.

6.5.1.2.2 February 1990

A variable pattern was common among depth profiles for cores collected in February 1990. Only BR8 showed a strong similarity of PAH pattern between the two collections. The following discussion refers to Figures 6.31 and 6.32 and Tables D.50 - D.55.

BR2: The depth profile for BR2 showed a maximum in both alkylated PAH and total HC at 5-10 cm, with PAH values otherwise low and total HC increasing again at the bottom, 30-32 cm. Total HC concentrations were similar to the core taken in February 1989, averaging 100,000 ppb. The FFPI dropped at 30-32 cm due to a slight rise in parent PAH concentrations and decreased presence of alkylated PAH. Naphthalenes composition averaged 62% of total PAH. Naphthalenes were typically lower in composition in the surface section, 38%, while phenanthrenes were more abundant, 26%, compared to lower sections. Weathering of hydrocarbons appeared to increase with depth; the ratio R/T averaged 0.23 in the top three sections and 0.10 in the remaining sections. This was consistent with the observed decrease in alkylated PAH with depth.

BR4: Two sections, 2-5 cm and 10-15 cm, showed high concentrations of both alkylated PAH and total HC compared to other sections of the core. All concentrations decreased to low or trace levels below the 20-25 cm section. The FFPI averaged 0.91 for the 0-20 cm sections, and R/T ratios averaged 0.16. Naphthalenes averaged 71% of total PAH with a low of 59% in the surface section. Average total HC concentration was 160,000 ppb, considerably lower than the average of 410,000 ppb observed in the February 1989 core. Alkylated PAH concentrations were roughly similar between February collections for the top half of the cores, but the patterns were opposite in the bottom sections, with the 1989 core showing increased concentrations compared to the surface, while no alkylated PAH was detected in the bottom sections of the 1990 core.

BR6: This core showed a profile with a decrease from surface levels, then a maxima in the central portion followed by a general decrease toward the bottom sections. The maximal concentrations of alkylated PAH and total HC did not coincide; alkylated PAH were highest, 12,000 ppb, in the 10-15 cm section, while total HC were most abundant, 390,000 ppb, in the 15-20 cm section. Parent PAH concentrations were also maximal in the 15-20 cm section and accounted for a decrease in FFPI. The FFPI pattern was the inverse of the total HC pattern. This was an indication that hydrocarbon inputs at areas of highest concentration were not of petrogenic origin. The average of the FFPI was 0.74, still fairly high; we concluded that the

sediment at this station had been subjected to multiple inputs from various sources. R/T values averaged 0.14, showed a decrease from a surface high of 0.23 to the bottom section at 0.07 and indicated a greater extent of weathering with depth. Total HC averaged 180,000 ppb compared to 120,000 ppb for February 1989. Alkylated PAH averaged 7,000 ppb, twice the average for 1989. Naphthalenes composition averaged 63% while phenanthrenes averaged 10% of total PAH.

BR8: Similar to the core analyzed for February 1989, this depth profile showed a pattern of alternating high and low values, although the areas of higher concentration were dissimilar between years. Alkylated PAH averaged 4,900 ppb compared to the 5,500 ppb in the 1989 core. The pattern for total HC was somewhat different than for the 1989 core, with a decrease in concentration around the 10-15 cm section, an increase at the 25-30 cm section followed by a decrease in the 30-35 cm section. The average total HC concentration, 100,000 ppb, was similar to the 1989 average, 130,000 ppb. FFPI values averaged 0.87 showing a more stable pattern than in 1989. R/T values averaged 0.18 and fell from a high of 0.32 at the surface to a low of 0.02 at 25-30 cm. Naphthalenes averaged 70% of total PAH, rose from a surface value of 44% to 85% at 15-20 cm, then dropped again slightly.

BR9: The variable pattern observed in BR8 was even more pronounced at BR9 for both alkylated PAH and total HC, while the FFPI was uniform at an average of 0.92. The patterns are somewhat similar to the 1989 core, with minimum values found at 15-20 cm and high concentrations found nearer the bottom. Average concentrations were 310,000 ppb total HC and 18,000 ppb alkylated PAH, both approximately double the averages for 1989. Naphthalenes showed a pattern similar to BR8, averaging 69% of total PAH with a low of 42% at the surface, and a high value of 80% found at 10-15 cm. This was not consistent with the pattern of PAH composition from 1989, which remained stable throughout the core. R/T averaged 0.21, with a low value of 0.13 at 15-20 cm, coinciding with low values in PAH and total HC concentrations.

BR11: The depth profile for total HC in this core was similar to the one for February 1989, with a subsurface decrease, followed by an increase in concentration at 20-25 cm. This core differed from the core for 1989 in that the surface section showed the highest concentration of both total HC and alkylated PAH. Average concentrations were 940 ppb and 47,000 ppb for alkylated PAH and total HC, respectively, the lowest averages among stations in the 1990 collection, and lower than the average for the same station in 1989. A significant increase in parent PAH concentration at 25-30 cm, with a corresponding decrease in FFPI value, was due to 4-ring compounds, including fluoranthene, pyrene, chrysene, benzo(b)fluoranthene and benzo(a)pyrene. FFPI averaged 0.40, ranging from 0.81 at 20-25 cm to 0.02 at 25-30 cm, adjacent sections. R/T values averaged 0.1, decreasing from 0.16 at the surface to a low of 0.06 at the bottom of the core. Naphthalenes averaged 44% of total PAH where detected and were absent in the 10-15 cm section.

6.5.1.2.3 Summary and Comparison between 1989 and 1990

Depth profiles for 1989 showed a general pattern of a decrease in petrogenic contaminant levels in central portions of the core with an increase toward the bottom sections, often to levels higher than found at or near the surface sections. In contrast, depth profiles for 1990 showed maximal concentrations nearer the surface, and the pattern was more erratic. Data from BR8 produced similar profiles between the two years.

6.5.2 Trace Metals

6.5.2.1 Surficial Sediments

Trace metals with the highest concentrations observed in Bayou Rigaud sediments were Ba, Zn, and Pb (Tables E.5 - E.8). Overall, concentrations of Zn and Pb were one-half or less of Ba concentrations.

Transect 1: Barium concentrations were relatively constant among stations for February and May 1989 but were generally elevated at all stations except BR9 in October 1989 (Figure 6.33). The decrease in concentration at BR9 was also seen in the hydrocarbon data. The February 1990 samples produced similar values to the first three collections but showed a clear trend of increasing concentrations which maximized at BR9. Zn and Pb concentrations were similar to those found at transect 2 stations and showed no clear trends, with maxima at BR9, BR8 and BR11 for the May and October 1989 and February 1990 sample, respectively.

Transect 2: Similar to data for Pass Fourchon, Ba concentrations showed a good correlation with hydrocarbon data, with maximal values at BR3 in February and May 1989 and BR4 in October 1989 (Figure 6.34). A low value for Ba at BR3 in February 1990 did not correspond to hydrocarbon data and may be an erroneous observation, as the two surrounding sites, BR4 and BR2, showed increasing concentrations. Also, an increase in hydrocarbon concentrations seen at BR6 in the May 1989 sample was not seen in Ba data. The Ba value for BR7 in October showed an increase from the sample at BR6; this was also not reflected in the hydrocarbon data. Zn and Pb distributions were dissimilar to the Ba profiles. Maximal values were seen at BR6 for October 1989. In general, increases in concentrations of Zn and Pb were seen at stations BR6 and BR4 compared to stations more removed from the discharge site.

6.5.2.2 Vertical Profiles

Vertical sediment cores from BR2, BR4, BR6, BR8 and BR9 from February 1989 were analyzed (Tables E.19 - E.23). Ba, Zn and Pb showed the highest concentrations over all surface stations within each collection period. Figure 6.35 shows the depth profiles for each core for Ba, Zn and Pb. Trace metal profiles for Bayou Rigaud cores, in general, showed little similarity among the different metals or to the hydrocarbon data.

BR2: The pattern of metal concentrations was fairly uniform, with only Ba showing changes with depth. From approximately 250 ppm in the top two sections, concentrations of Ba rose to approximately 400 ppm in the 5-10 cm section and remained stable below that depth. This pattern did not coincide with the patterns seen for hydrocarbon data.

BR4: The pattern for trace metals in this core also did not coincide with the pattern for hydrocarbon data, with the exception of a slight rise in concentrations seen in the 2-5 cm section. Deeper sections decreased for Zn and Pb, while Ba concentrations continued to rise to a maximum near 600 ppm in the 20-25 cm section and then decreased in deeper sections.

BR6: Overall, levels of Ba were similar to those in BR2 and slightly lower than BR4. The only similarity between Ba and hydrocarbon data was a drop in Ba concentration in the 15-20 cm section, which coincided with a minimum in FFPI value. The profile for Zn, with a maximal value of 85 ppm in the 15-20 cm section, was similar to the parent PAH data. Ni concentrations also showed a secondary maximum in this section (data not shown). Although not easily seen when graphed on the same scale, Zn concentrations showed a nearly inverse pattern with Ba concentrations.

BR8: The profile for Ba in this core was similar to the hydrocarbon profile with a general increase with depth, although somewhat less variable than the hydrocarbon profile. Profiles for Zn and Pb were fairly uniform, with a small increase in the 2-5 cm section, which did not correlate to any of the hydrocarbon data.

BR9: This core showed the highest value of Ba in the Bayou Rigaud samples from February 1989, 900 ppm at 5-10 cm. The hydrocarbon data also showed maximal values in this section; however, highest concentrations of hydrocarbons occurred lower in the core, while Ba concentrations dropped to an average of 410 ppm below the 5-10 cm section. Other metals were

fairly constant in concentration throughout the core, with the exception of As, which had a maximal concentration of 39 ppm in the 10-15 cm section.

6.5.3 Radionuclides

6.5.3.1 Surficial Sediments

Surficial sediment Pb-210 concentrations in the Bayou Rigaud study area exhibited similar spatial patterns for each of the four sample periods (Figures 6.36 - 6.39, Table F.8). Pb-210 activities were highest in surface sediment stations proximate to the Conoco and Exxon discharge points and decreased uniformly away from the discharge sites. Surface Pb-210 activities ranged from 2.43 to 4.15 $\text{dpm}\cdot\text{g}^{-1}$ during February 1989, from 0.56 to 2.58 $\text{dpm}\cdot\text{g}^{-1}$ during May 1989, from 1.15 to 2.78 $\text{dpm}\cdot\text{g}^{-1}$ during October 1989 and from 1.11 to 1.87 $\text{dpm}\cdot\text{g}^{-1}$ during February 1990. While quality and quantity of particle surface sites available for Pb-210 sorption is determined largely by grain size and organic content, surface sediment Pb-210 activities did not correlate with percent organic carbon content and grain size. This may be the case at Bayou Rigaud because the clay content of the sediments never exceeded 7%. Surface sediment Pb-210 activities in coastal environments are typically about 2.0 $\text{dpm}\cdot\text{g}^{-1}$ (range: 0.1 to 5.0 $\text{dpm}\cdot\text{g}^{-1}$), depending on many factors controlling the sorption reactions (e.g., grain size, percent organic carbon, turbidity in overlying waters). The surface sediment Pb-210 activities observed at Bayou Rigaud were at or just above the upper limit for activities found in natural environments.

6.5.3.2 Vertical Profiles

Sediment Pb-210 activities within the upper 10-50 cm (length of the cores collected) increased or remained the same in a down-core direction. This is different from natural environments where Pb-210 sediment activities decrease down core due to decay, and reach a constant background level (~ 0.1 to $0.5 \text{ dpm}\cdot\text{g}^{-1}$). Decreasing Pb-210 activities with depth in the core is a prerequisite for calculating sedimentation rates; since these conditions were not present, sedimentation rates could not be calculated for Bayou Rigaud (see Section 3.6). The pattern observed in cores at Bayou Rigaud indicated that Pb-210 supply to the sediments greatly exceeded decay (Figure 6.40). Because the Pb-210 activities do not decrease to a background level in the Bayou Rigaud cores, the inventories calculated from these cores give a minimum estimate of the Pb-210 flux to the area (Tables F.9 - F.10). During February 1989, minimum Pb-210 sediment inventories ranged from 66.5 to 154.1 $\text{dpm}\cdot\text{cm}^{-2}$. These inventories indicated Pb-210 fluxes of more than 2.0 to 4.8 times greater than natural supply. During May 1989, minimum Pb-210 sediment inventories ranged from 29.8 to 76.2 $\text{dpm}\cdot\text{cm}^{-2}$, indicating fluxes of more than 1.0 to 2.4 times greater than natural supply. During October 1989, minimum Pb-210 sediment inventories ranged from 40.0 to 81.5 $\text{dpm}\cdot\text{cm}^{-2}$, indicating fluxes of more than 1.3 to 2.5 times greater than natural supply. During February 1990, minimum Pb-210 sediment inventories ranged from 29.1 to 79.7 $\text{dpm}\cdot\text{cm}^{-2}$, indicating fluxes of more than 1.0 to 2.5 times greater than natural supply.

6.6 Benthic Biota

The benthic infauna of the Bayou Rigaud study area was a combination of marine and intermediate salinity organisms. The dominants of the benthic community were the polychaete, *Streblospio benedicti*, and the bivalve, *Mulinia lateralis*. *Streblospio benedicti* was abundant in all seasons, but most numerous in the February collections of 1989. In general, *Mulinia lateralis* outnumbered *Streblospio* in February 1990 as the dominant recruitment organism. Numerous other polychaetes, bivalves, gastropods, nemertean worms, oligochaetes and pericaridean crustaceans were also collected. The Bayou Rigaud study site had, by far, the most diverse fauna of all the study areas (Table G.7).

There were significant differences among the stations for most of the benthic community parameters for all of the sample dates. There were no stations where the benthic fauna were consistently and persistently depressed in number of species or individuals. These results were inconsistent with those reported in the earlier study (Boesch and Rabalais 1989a) where no or reduced species were collected from sediments near the Conoco discharge and reduced species were collected from near the Exxon discharge. During the Boesch and Rabalais (1989a) study, however, the sediments were likely sampled closer to the discharge points.

While there were no severely depressed fauna, there were indications, however, that some of the stations (BR3, BR4, BR5, BR7 and BR8) had fewer species and individuals than the other stations (Figures 6.41 - 6.44); these stations were near or opposite a discharge point. Reduced fauna at these stations was not consistent through time. Station BR9, however, did not have consistently fewer species and individuals, and it was located opposite a discharge point.

In February 1989, there were significant differences among stations with respect to number of species, diversity and evenness, but there was considerable overlap in the means of the parameters (Tables 6.2, G.8). Differences among the stations were more obvious for all benthic community parameters in the October 1989 and February 1990 collections (Tables 6.4, 6.5, G.10, G.11). In May 1989, when additional stations were sampled, there were significant differences among stations but considerable overlap in the means for the parameters. In May 1989 there were no obvious trends in community structure related to distance from a discharge point (Tables 6.3, G.9).

The co-analysis of variance for all sample periods combined for 11 stations showed significant differences between stations for all dates combined and significant differences between dates for the combined station data (Tables 6.5, G.12). The analysis showed that there were real differences among the stations, but that seasonal effects were also important in the variance among stations.

The benthic community parameters of number of species and individuals were not related to the grain size distribution of Bayou Rigaud stations. There was a relationship with the total organic carbon of the sediments, with the number of individuals being greater in sediments with higher organic content (Figure 6.45). The sample date was an influential factor on both the number of species and individuals, as shown in the co-analysis of variance. Numbers were higher in both of the February samples, reduced in May and lowest in October. In stepwise multiple regressions of environmental parameters important in determining the variation in number of species and individuals, the sample date was the first factor identified. With regards to number of species, there was only one more factor identified in the stepwise multiple regression as being important in explaining the variation among the means; this was sediment barium concentration. Sediment Ba concentration and total organic content were identified in the stepwise multiple regression for number of individuals as significant factors explaining the variation.

Non-linear relationships with several sediment chemical constituents identified threshold values above which number of species or number of individuals were usually depressed below background levels (Table 6.7). There were no observed threshold levels of chemical constituents in near-bottom waters above which the benthic fauna was depressed.

6.7 Summary

The Bayou Rigaud study area, which receives a total discharge of $146,000 \text{ bbl}\cdot\text{d}^{-1}$ produced waters from two discharges, is a well-flushed, saline system near a major pass to the Gulf of Mexico. Shear velocities exceeded $0.01 \text{ m}\cdot\text{s}^{-1}$ for much of the tidal record on both flood and ebb tides. The magnitude of shear velocities recorded from Bayou Rigaud indicates that sediment entrainment is possible. Still, for half of the study period sediments were composed primarily of silts indicating that sediment deposition does occur. A major shift in the sediment grain size distribution from primarily sands in February and May 1989 to primarily silts in

October 1989 and February 1990 suggests that major disruptions are possible in the sediment bed and that periods of accumulation are likely to follow. The water column in Bayou Rigaud varies from well-mixed to stratified. No evidence of elevated bottom water salinities associated with the produced water effluents was recorded. In a previous study (Boesch and Rabalais 1989a), only one station near the Conoco access canal exhibited higher than ambient bottom water salinity.

Water column contaminants in the form of volatile organic hydrocarbons in near-bottom waters were uniformly low ($< 10 \mu\text{g}\cdot\text{l}^{-1}$) with the exception of the BR4 sample in October 1989. Even this maximum ($110 \mu\text{g}\cdot\text{l}^{-1}$) did not approach the levels detected in near-bottom waters in the previous study (Boesch and Rabalais 1989a) which were nearly an order of magnitude higher. Higher values in the previous study could be attributed to (in one instance but not both) sampling methodology. Total PAH and total saturated HC in near-bottom water were also higher at one station in the previous study than in any of the stations sampled in the current study. These discrepancies point to differences in the loading of produced water hydrocarbons to Bayou Rigaud between the previous and current studies and/or differences in the mixing and dispersion of the organics upon discharge to the receiving environment. Pb-210 and total radium activities were identifiable in the near-bottom waters to a distance of up to 200 or 300 m from either discharge point.

The PAH and total HC concentrations in surficial sediments were elevated above background levels as far as 1300 m from the largest discharge (station BR4) or as much as 500 to 800 m from either of the two discharge points. Comparison of parent PAH data, alkylated PAH data and FFPI values indicates a produced water source of contamination in sediments to as much as 500 m from either of the two discharge points. As noted above for near-bottom waters, the maximal values for surficial sediment contaminants of total PAH and total saturated HC were higher in the previous study (Boesch and Rabalais 1989a); but, overall, concentrations of sediment chemical constituents were similar between the previous and current studies. Pb-210 activities were highest in surficial sediments at stations adjacent to the two discharge points and decreased uniformly away from each. Elevated levels were detected as far as 1000 m from the largest discharge. Differences in concentrations of various chemical constituents were obvious in the eastern part of the study area adjacent to the Conoco discharge (stations BR3, BR4 and BR5) but were minimal in the western part of the study area (stations near BR9 and the Exxon discharge). Temporal variability could be attributed to differences in hydrocarbon loading and treatment efficiency, major shifts in sediment grain size composition, disruption of the sediment bed and subsequent periods of accumulation, and variability in station location. Vertical sediment cores which were analyzed for six stations for two collection periods indicated high levels of hydrocarbon contaminants in the surface or subsurface layers as well as near the bottom of the core at 25 to 35 cm with less between. There were exceptions to this general rule as well as less definitive trends for various constituents. Distribution of the various constituents were generally not consistent between the two collection periods analyzed. Pb-210 vertical profiles indicated that the flux of Pb-210 to this environment far exceeded the natural decay rate. The inventories calculated from these cores showed a Pb-210 flux in February 1989 that was twice that of any of the subsequent collection periods. This apparent sediment accumulation corresponds with higher chemical constituents in the surficial sediments of the eastern part of the study area for the same period.

There were significant differences among the stations for most of the benthic community parameters for all of the sample dates as well as significant seasonal differences. There were no severely depressed faunal communities in the Bayou Rigaud study area. There were stations that had a reduced number of species and, more obviously, a reduced number of individuals. These stations were adjacent to or near a discharge point, but reduced fauna at these stations was not consistent through time. Stations where species or individuals were reduced were identifiable by certain sedimentary characteristics, including higher organic content and elevated hydrocarbons and levels of Ba compared to background levels.

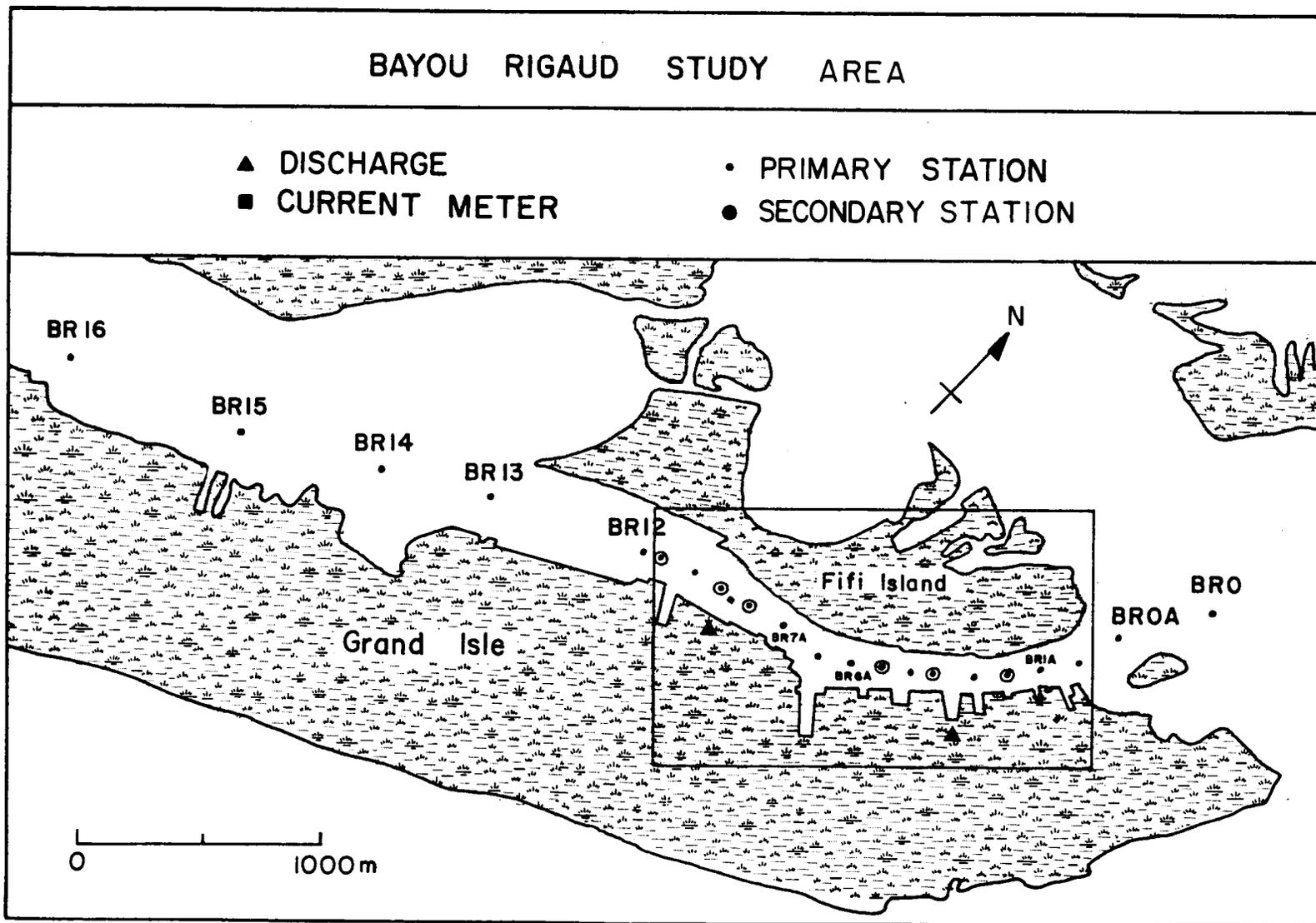


Figure 6.1. Bayou Rigaud study area with increased station coverage for May 1989. Station numbers labeled are stations sampled in May 1989 in addition to the stations shown in Figure 6.2.

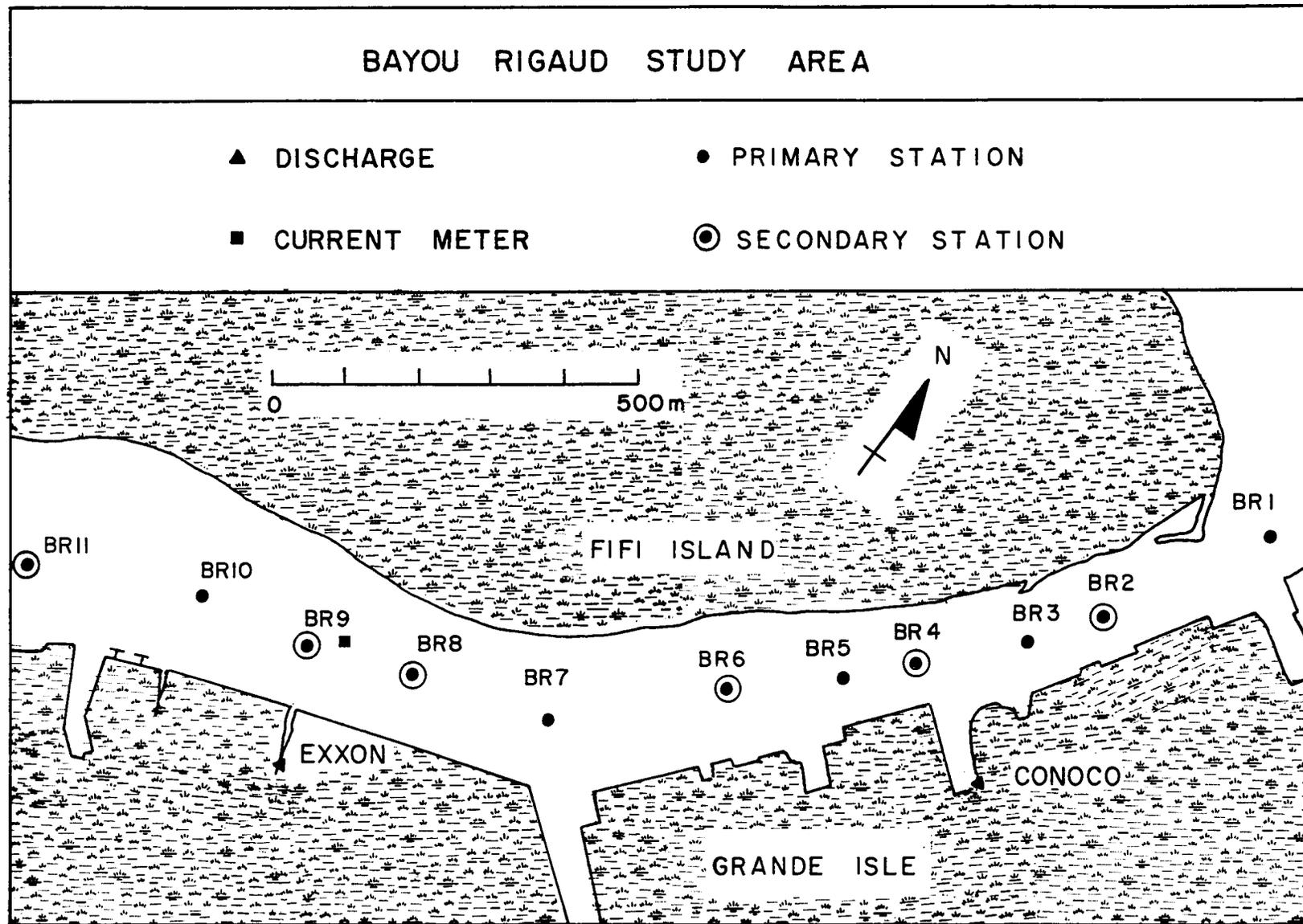


Figure 6.2. Bayou Rigaud study area for station coverage for February and October 1989, and February 1990.

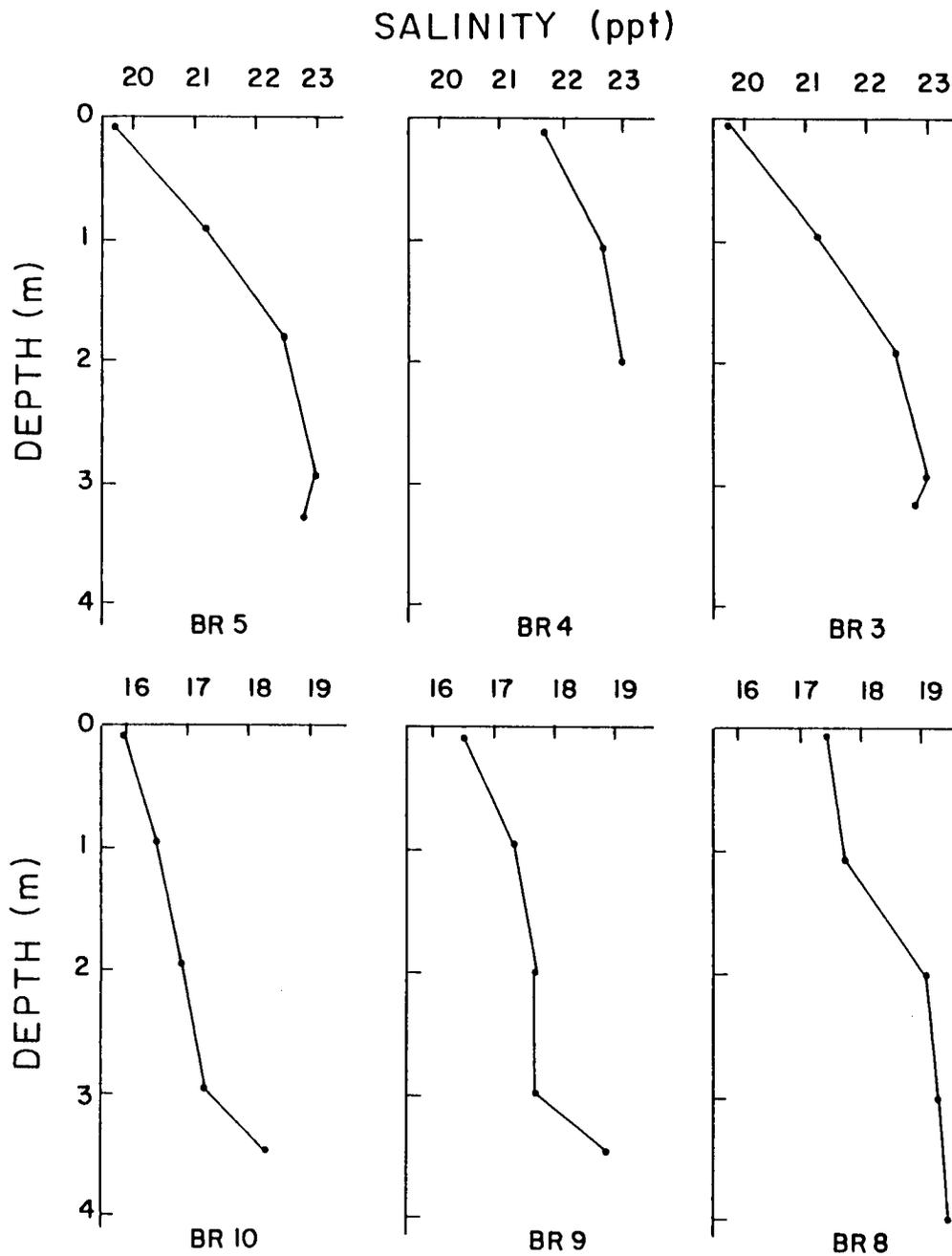


Figure 6.3. Salinity distribution through the water column at selected stations for Bayou Rigaud, February 1989.

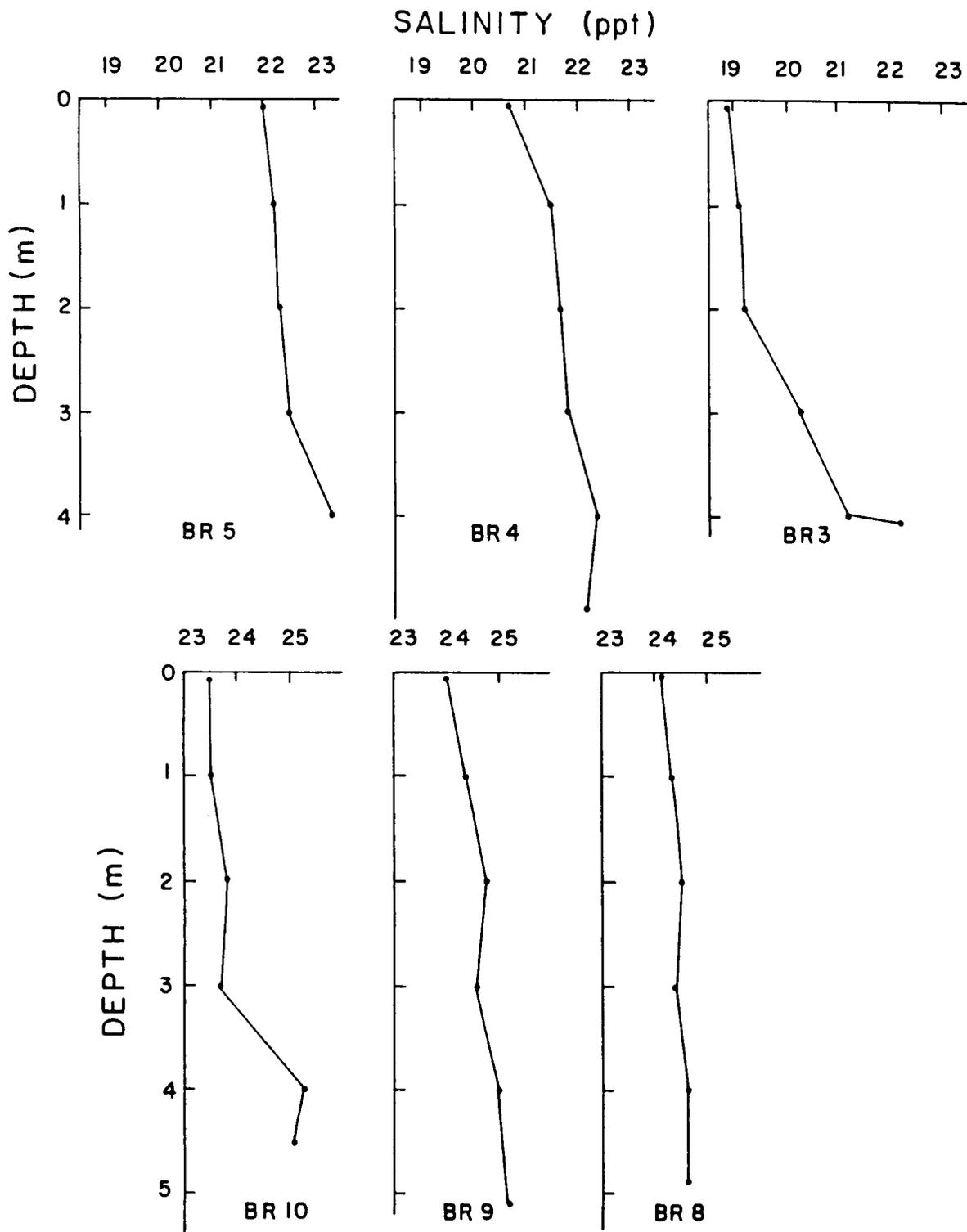


Figure 6.4. Salinity distribution through the water column at selected stations for Bayou Rigaud, May 1989.

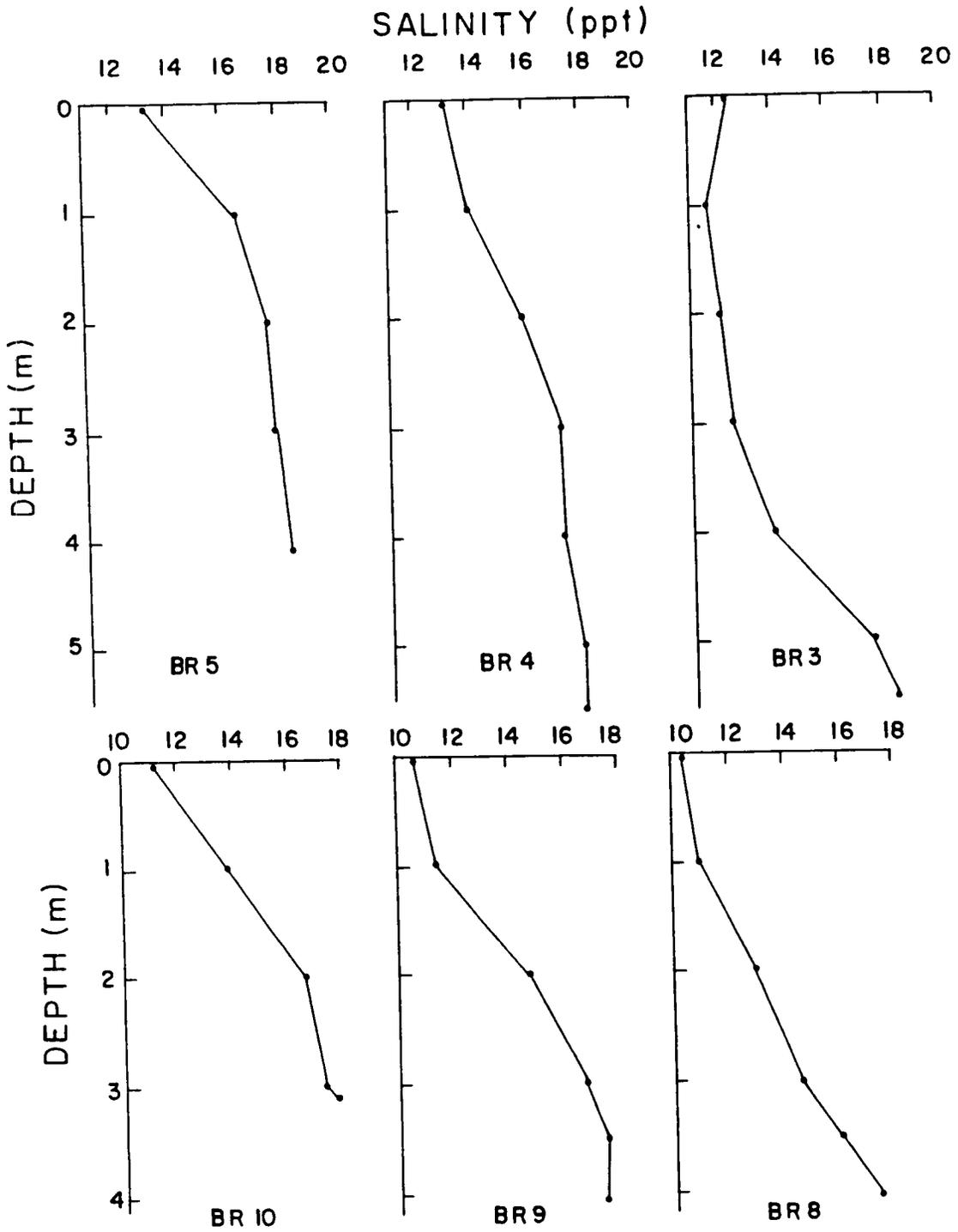


Figure 6.5. Salinity distribution through the water column at selected stations for Bayou Rigaud, February 1990.

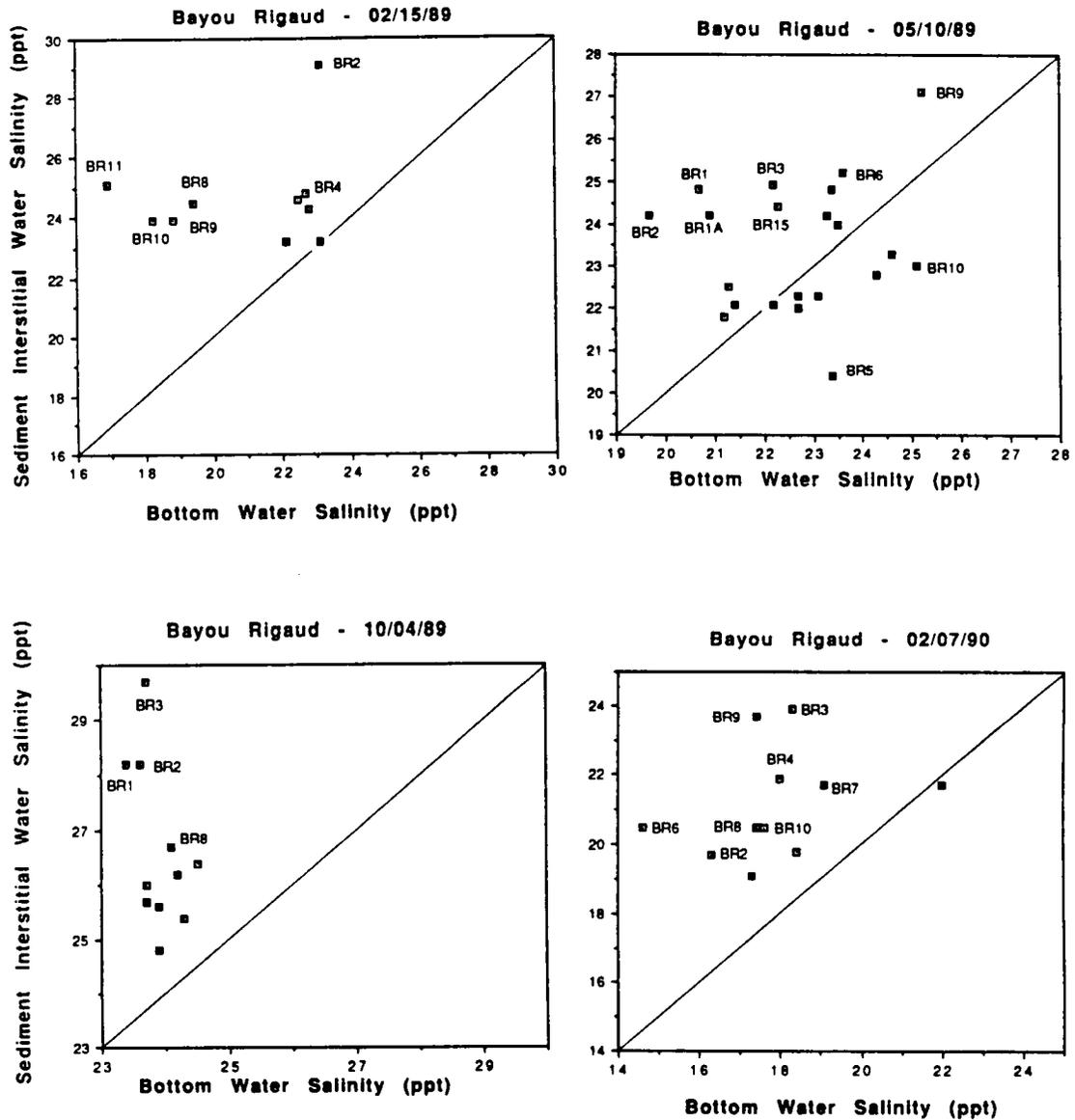


Figure 6.6. Comparisons of interstitial water salinity from surface sediments of stations in the Bayou Rigaud study area and near-bottom water salinity. Station number given for values most different from a 1:1 relationship (indicated by diagonal line).

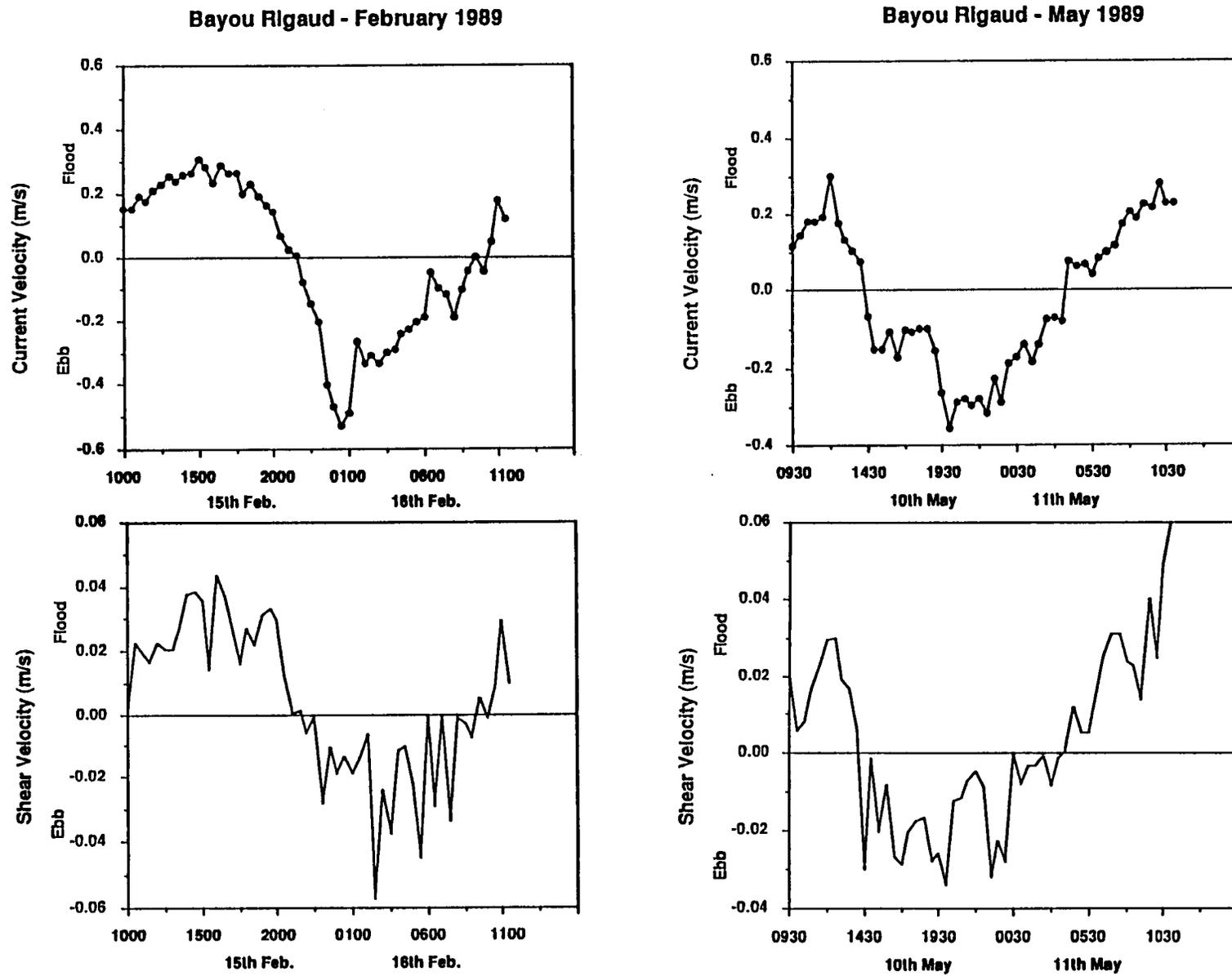


Figure 6.7. Mean tidal current velocity variation and calculated shear velocities for Bayou Rigaud, February and May 1989.

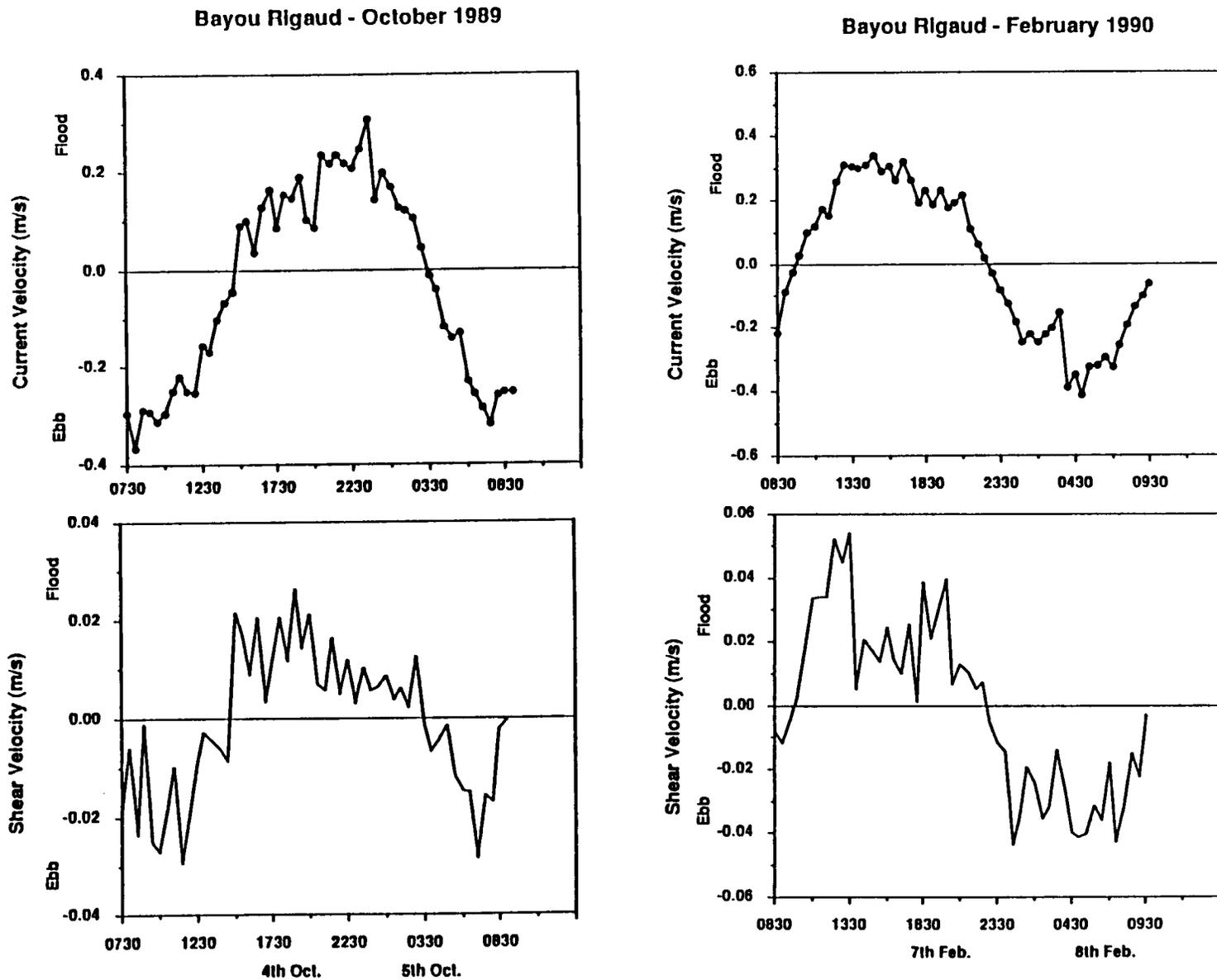


Figure 6.8. Mean tidal current velocity variation and calculated shear velocities for Bayou Rigaud, October 1989 and February 1990.

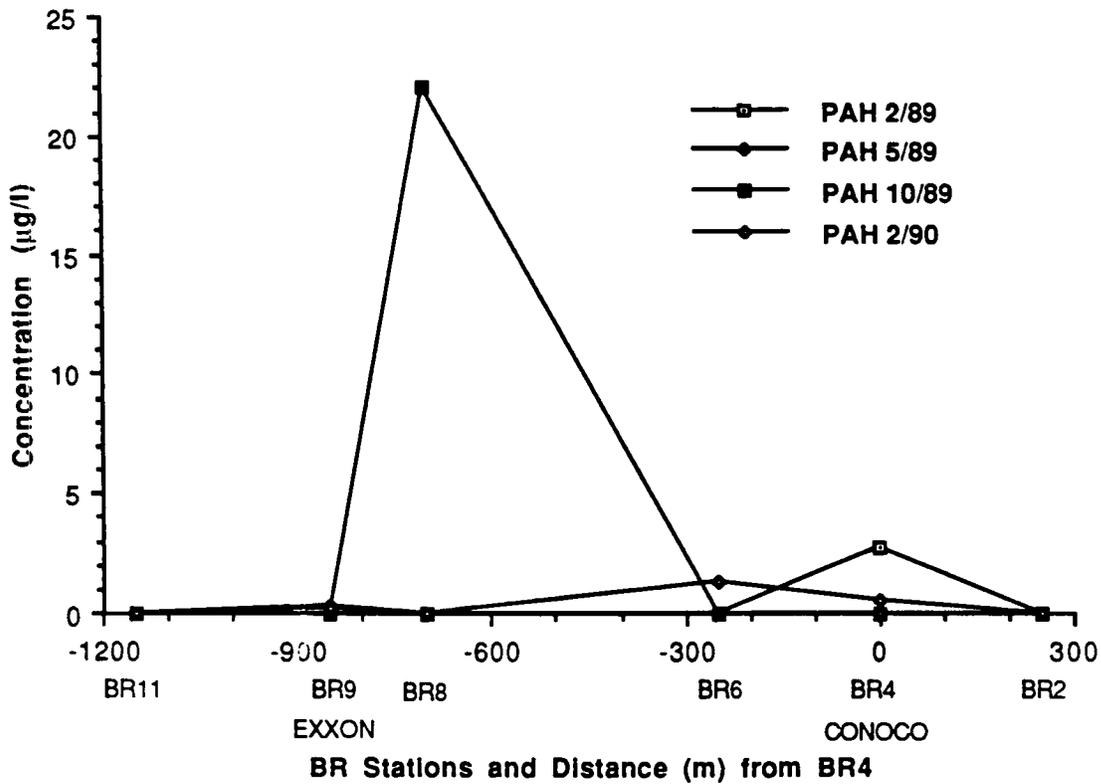
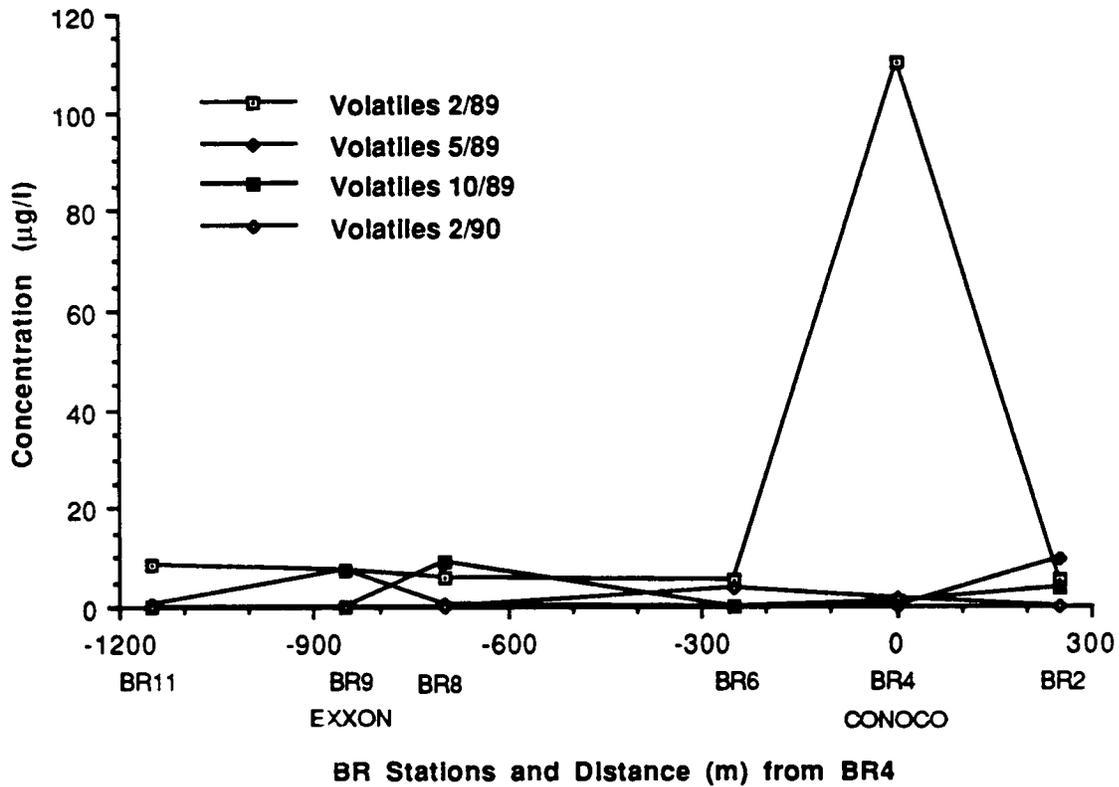


Figure 6.9. Spatial distribution of volatile hydrocarbon and PAH concentrations in Bayou Rigaud near-bottom waters for four sample periods.

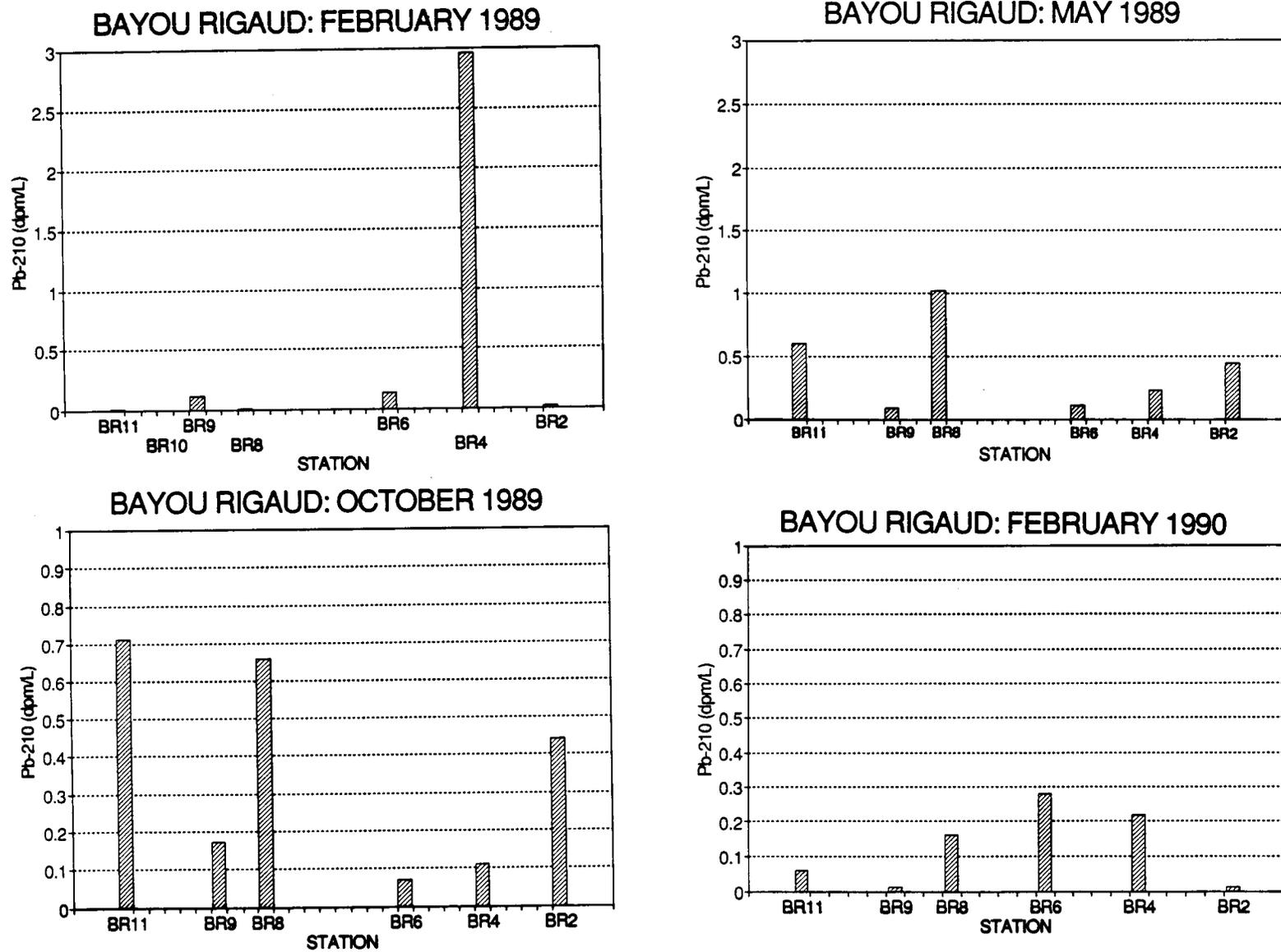


Figure 6.10. Spatial distribution of Pb-210 activities in Bayou Rigaud near-bottom waters for four sample periods.

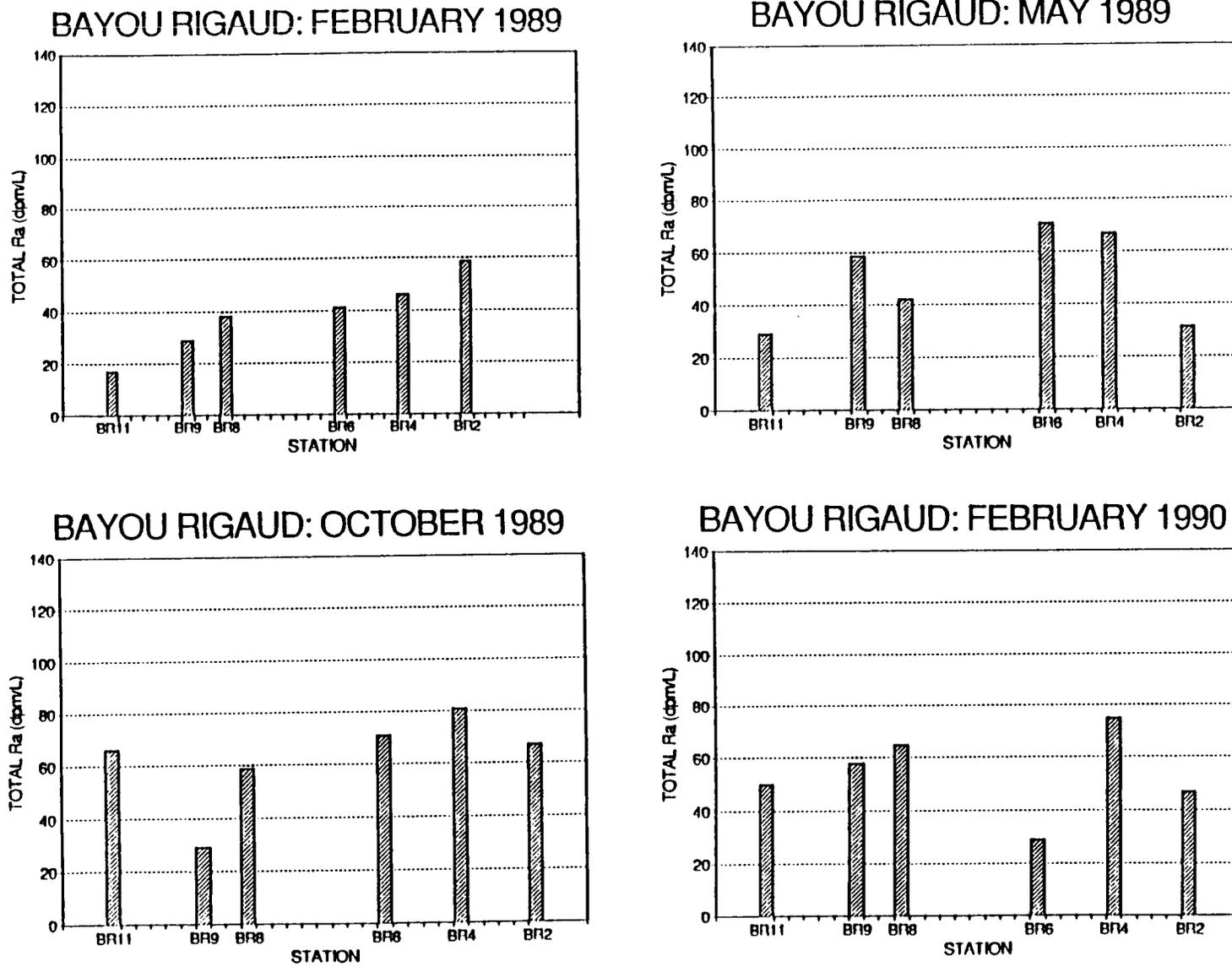


Figure 6.11. Spatial distribution of total radium activities in Bayou Rigaud near-bottom waters for four sample periods.

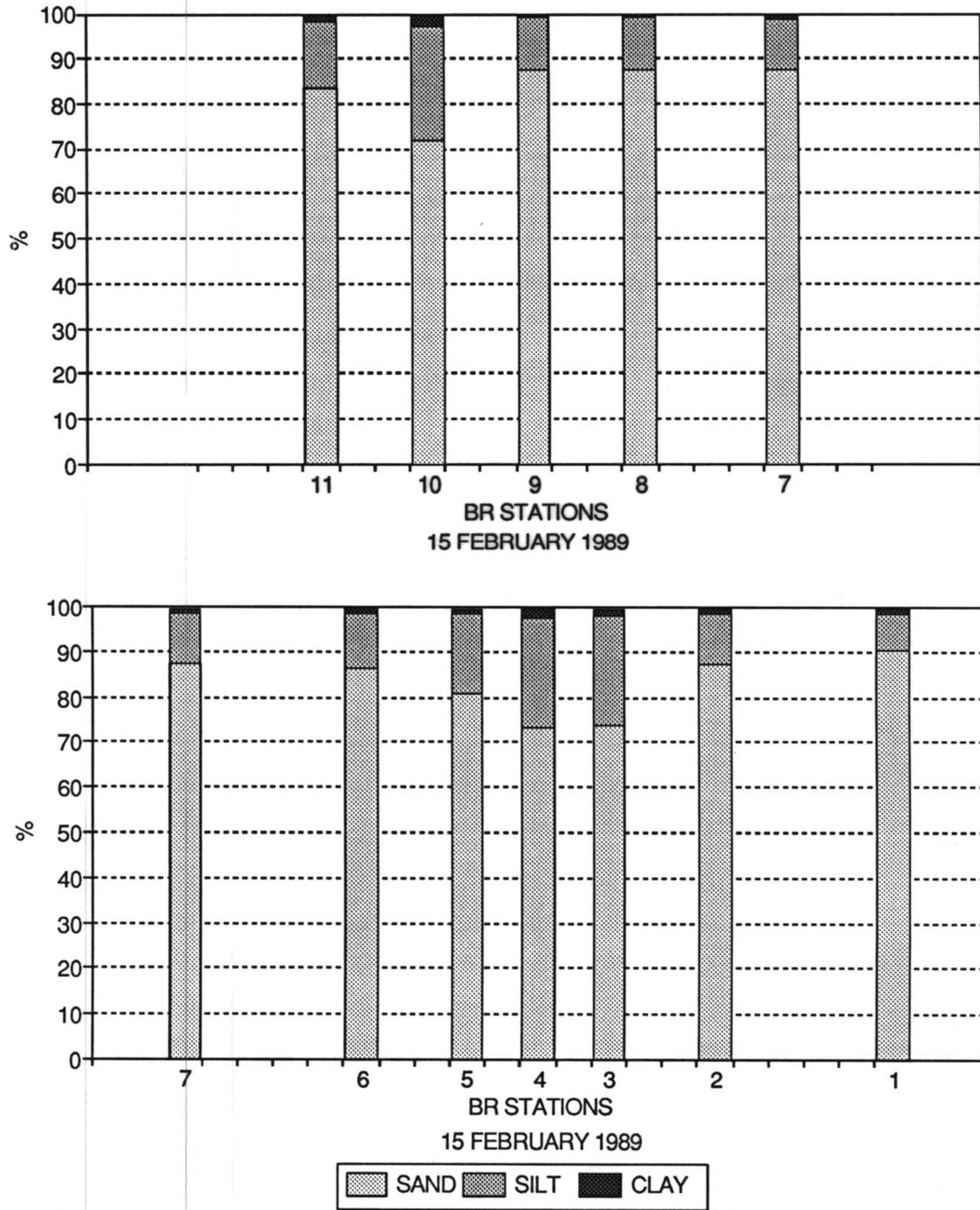


Figure 6.12. Spatial distribution of surface sediment grain size from Bayou Rigaud, February 1989.

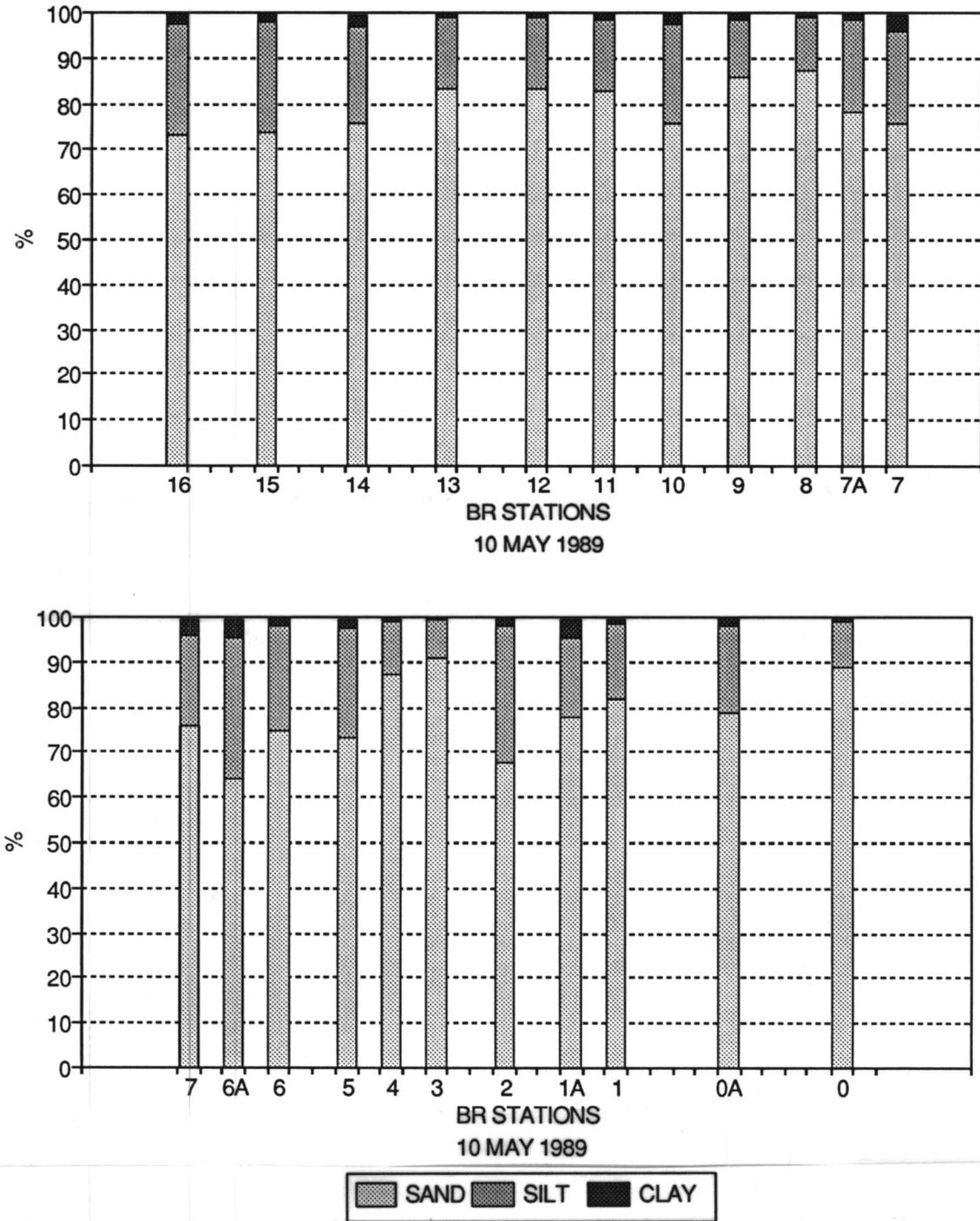


Figure 6.13. Spatial distribution of surface sediment grain size from Bayou Rigaud, May 1989.

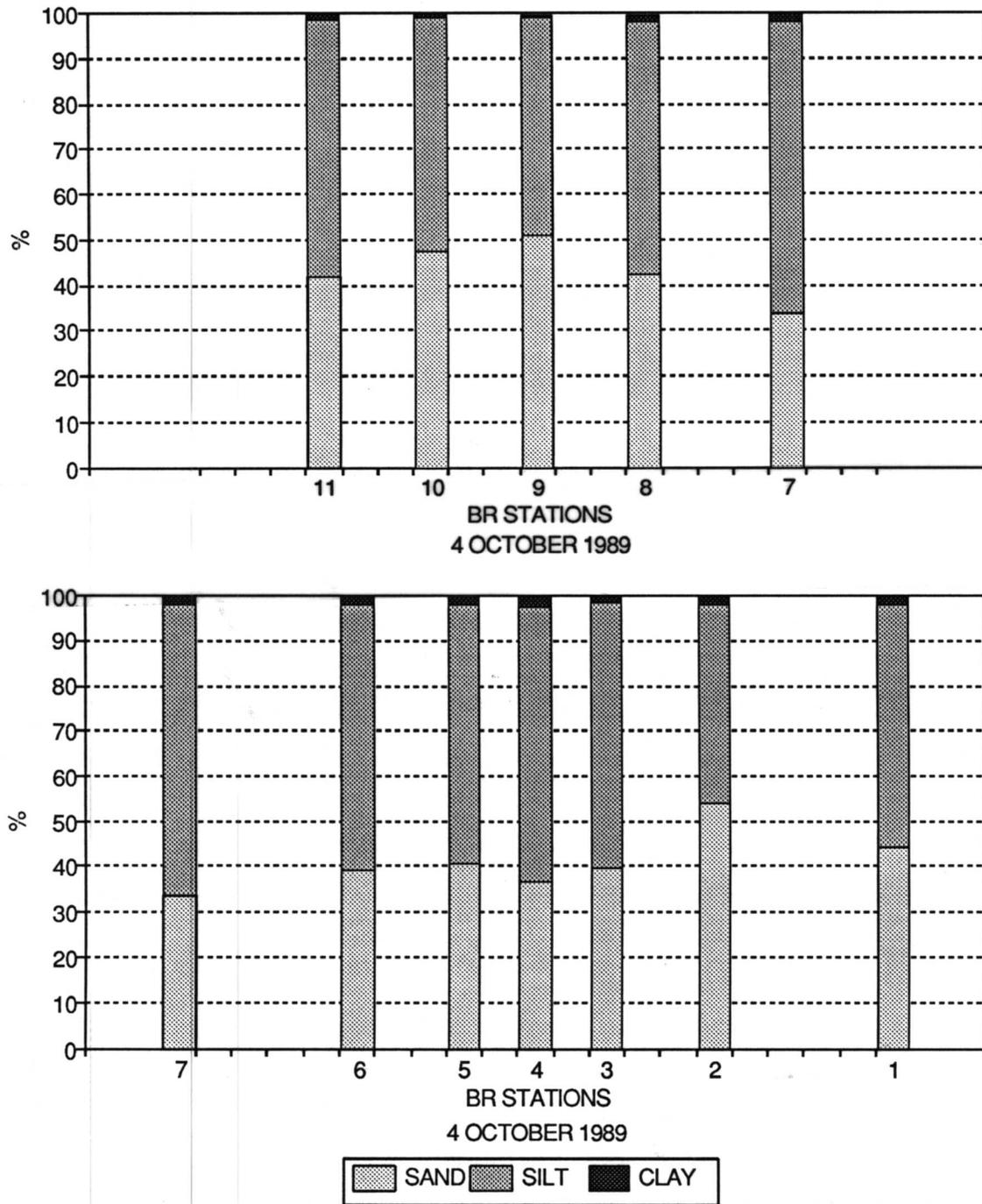


Figure 6.14. Spatial distribution of surface sediment grain size from Bayou Rigaud, October 1989.

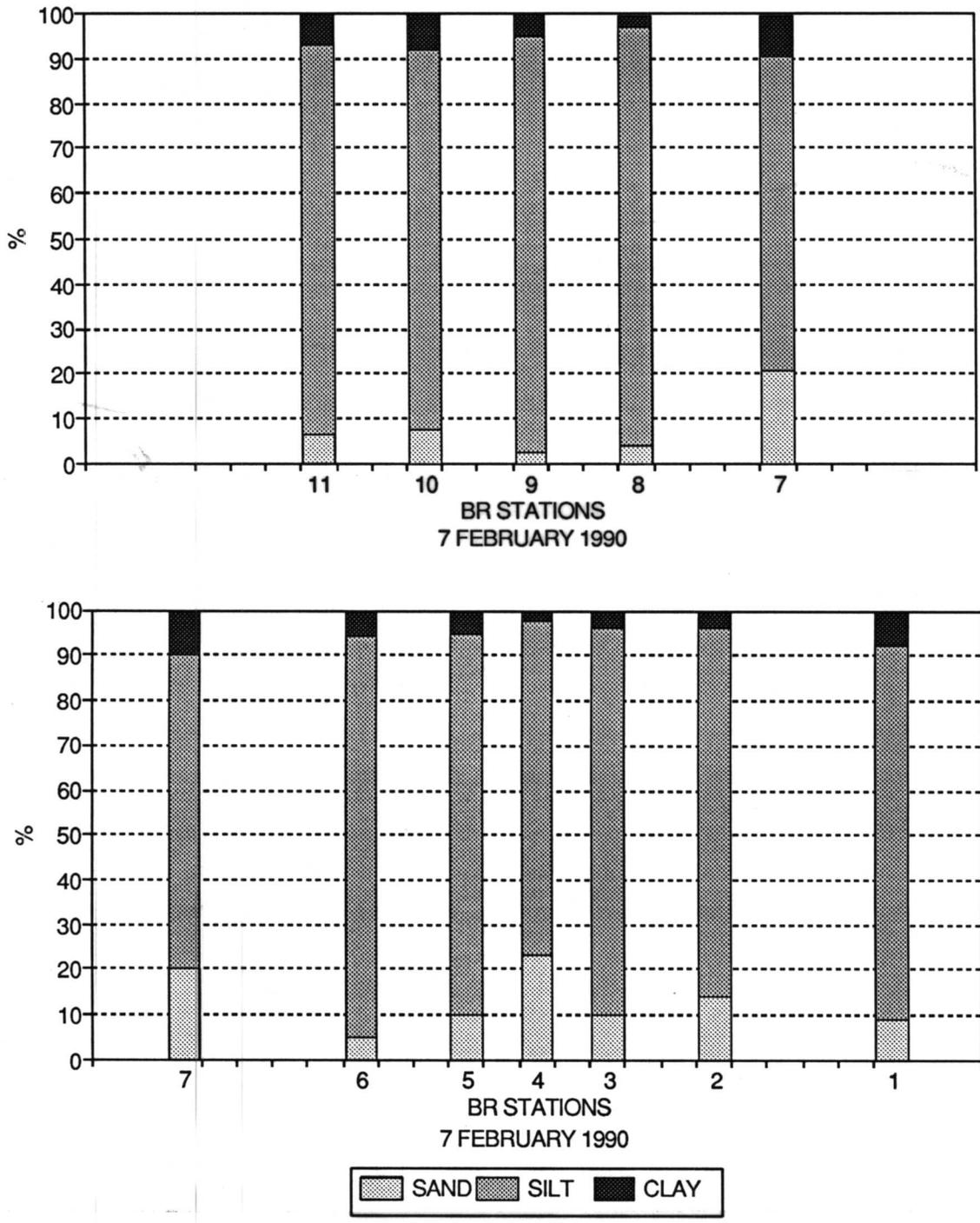


Figure 6.15. Spatial distribution of surface sediment grain size from Bayou Rigaud, February 1990.

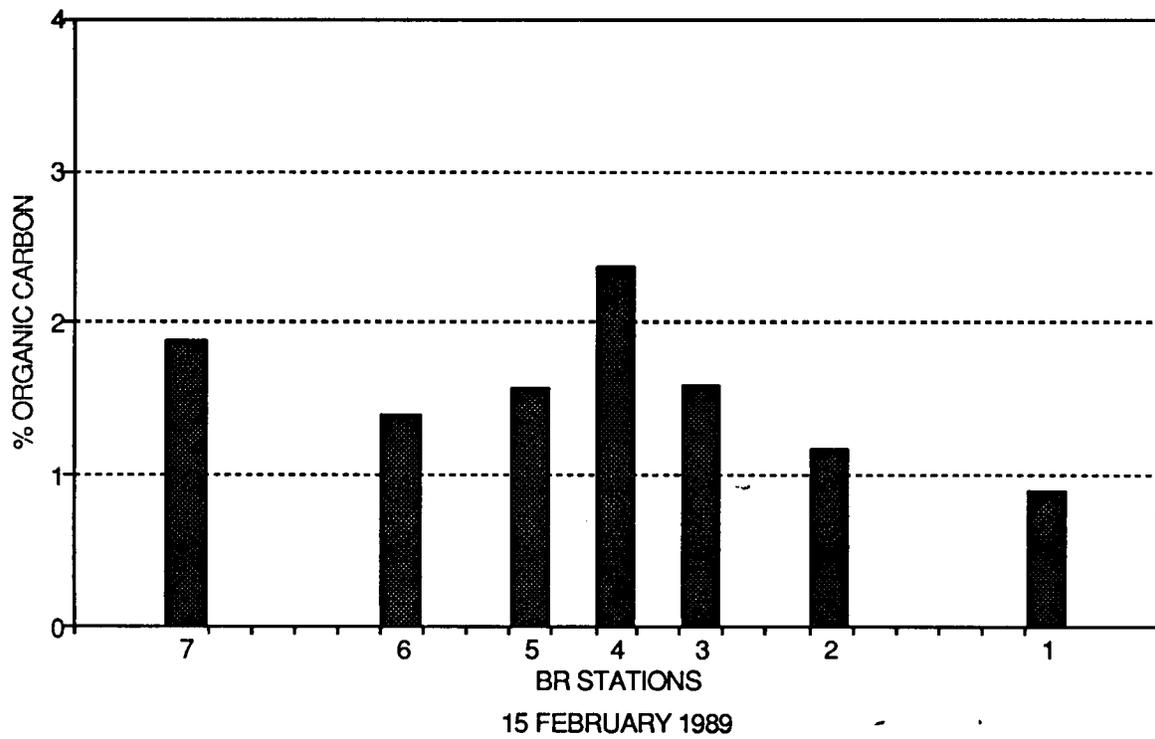
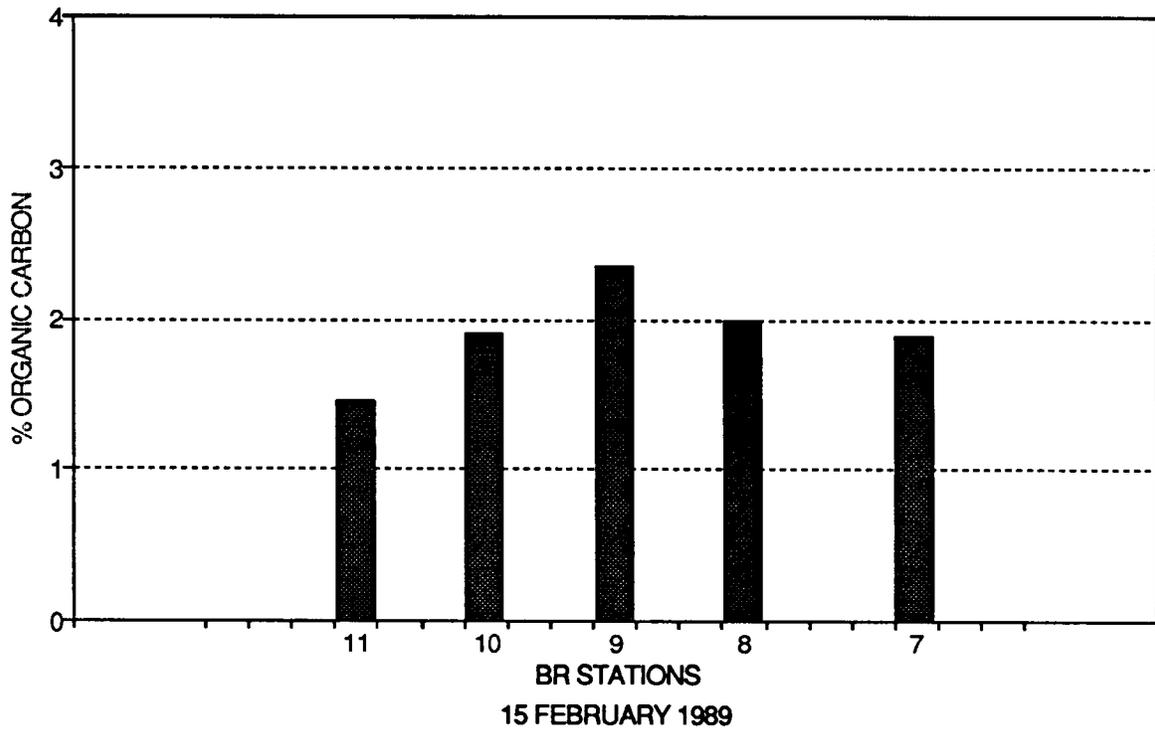


Figure 6.16. Spatial distribution of percent total organic carbon in surface sediments from Bayou Rigaud, February 1989.

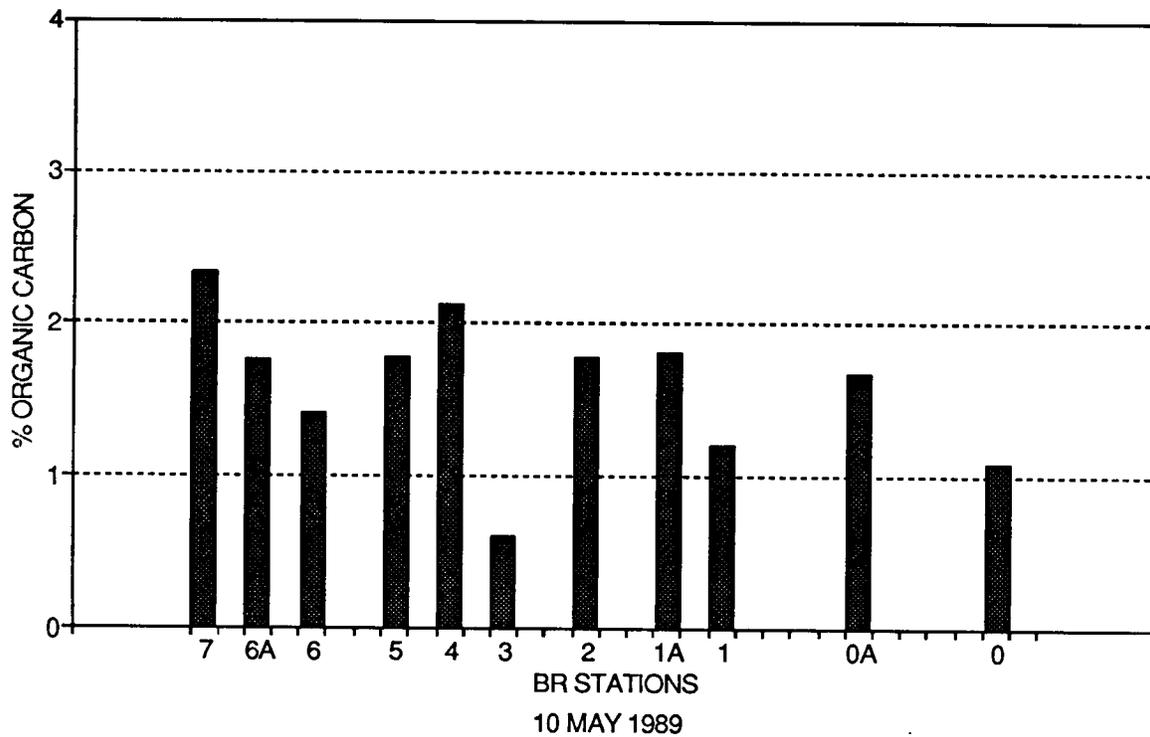
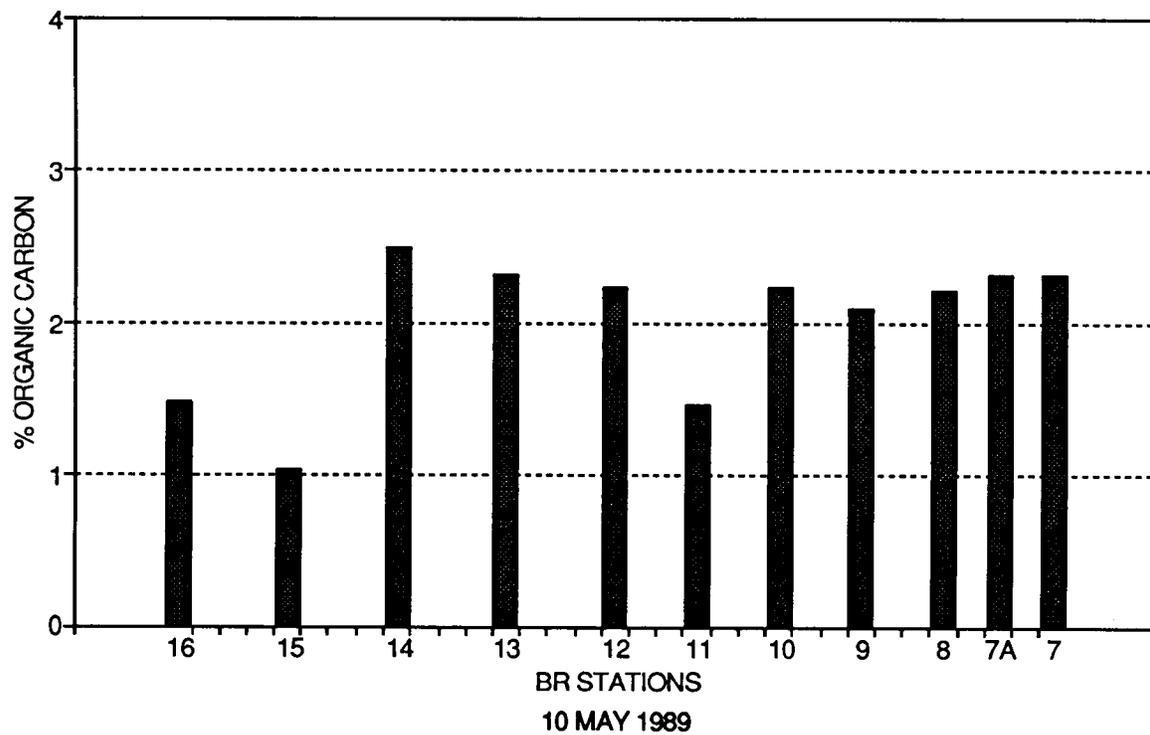


Figure 6.17. Spatial distribution of percent total organic carbon in surface sediments from Bayou Rigaud, May 1989.

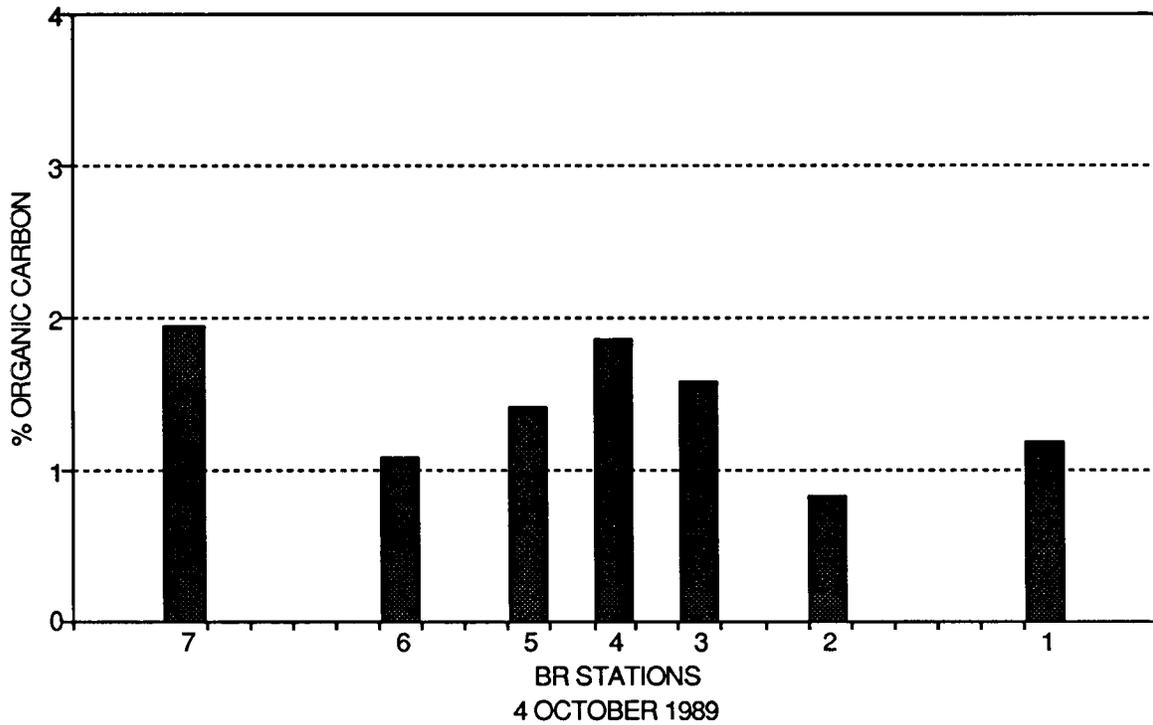
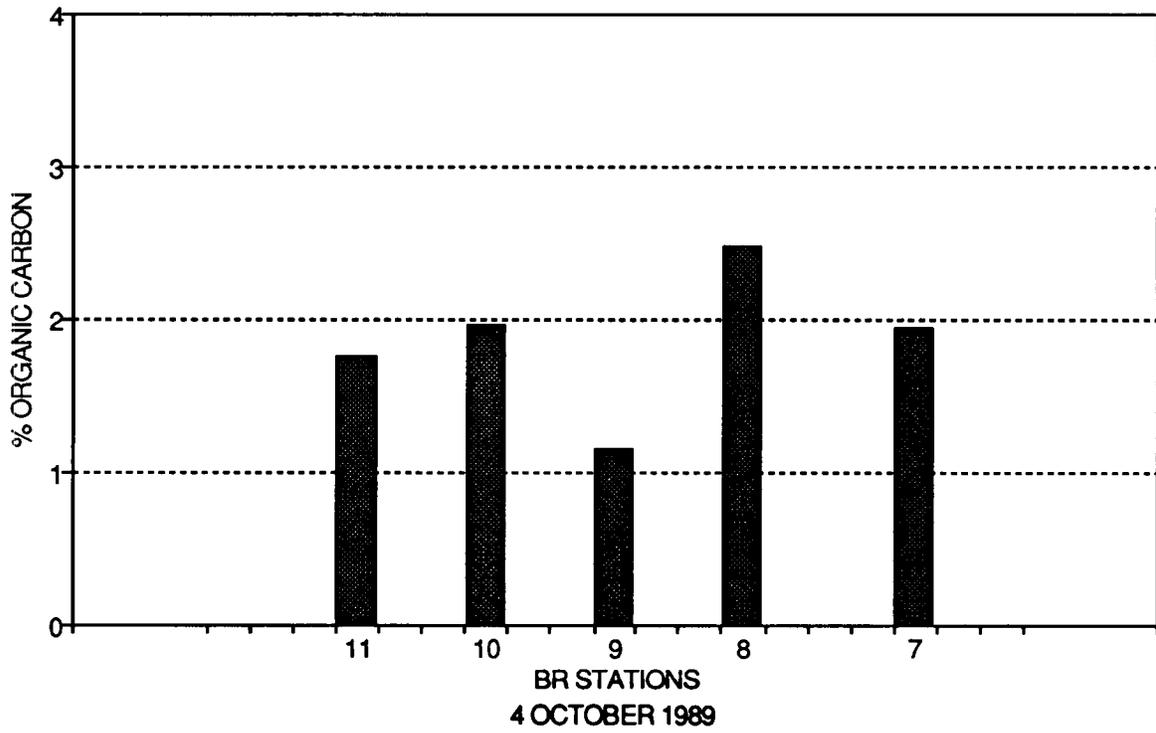


Figure 6.18. Spatial distribution of percent total organic carbon in surface sediments from Bayou Rigaud, October 1989.

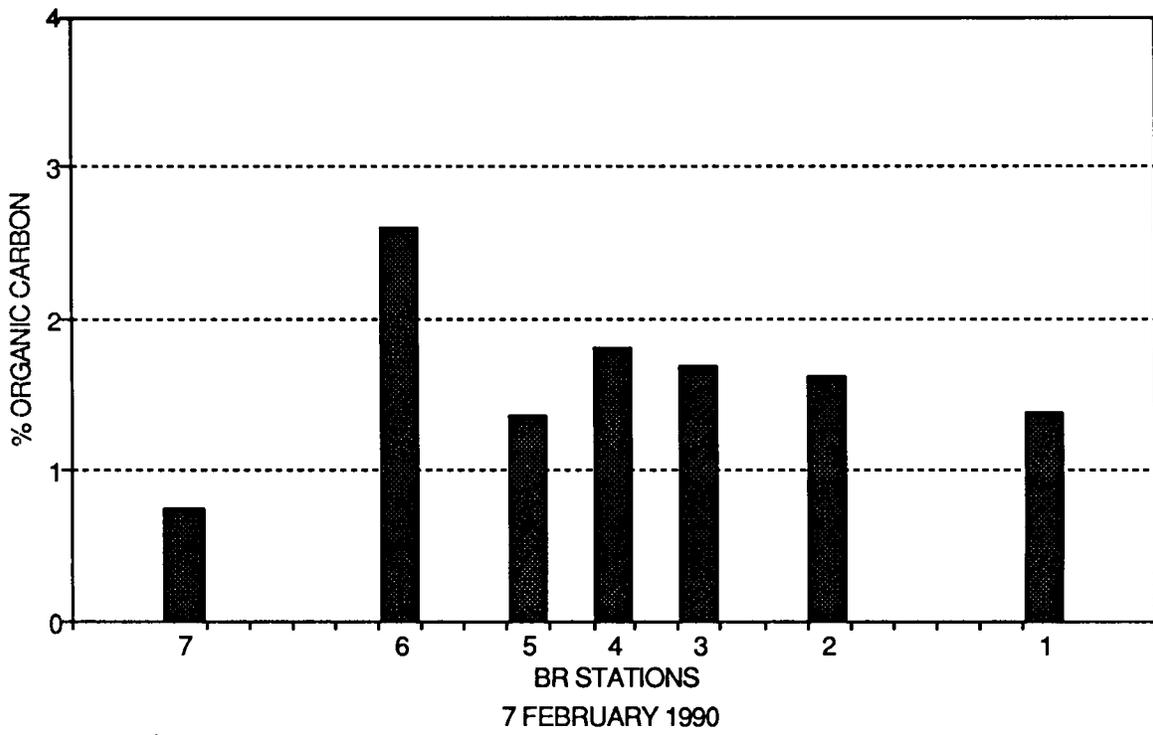
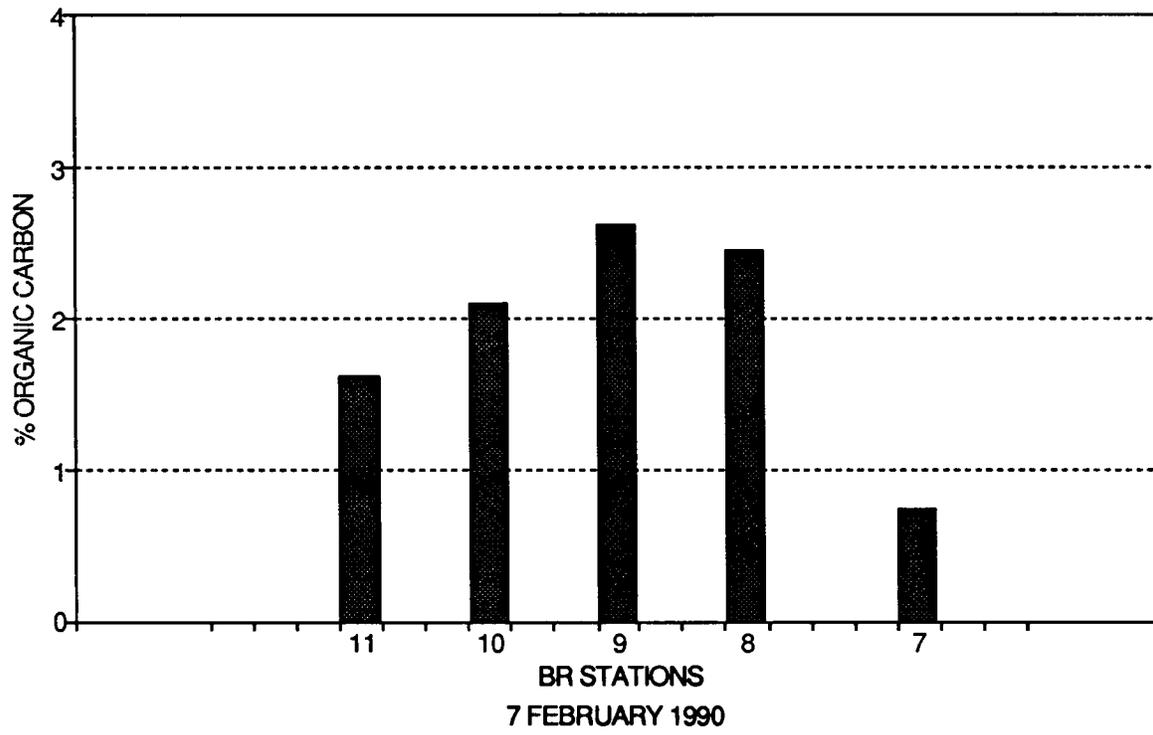


Figure 6.19. Spatial distribution of percent total organic carbon in surface sediments from Bayou Rigaud, February 1990.

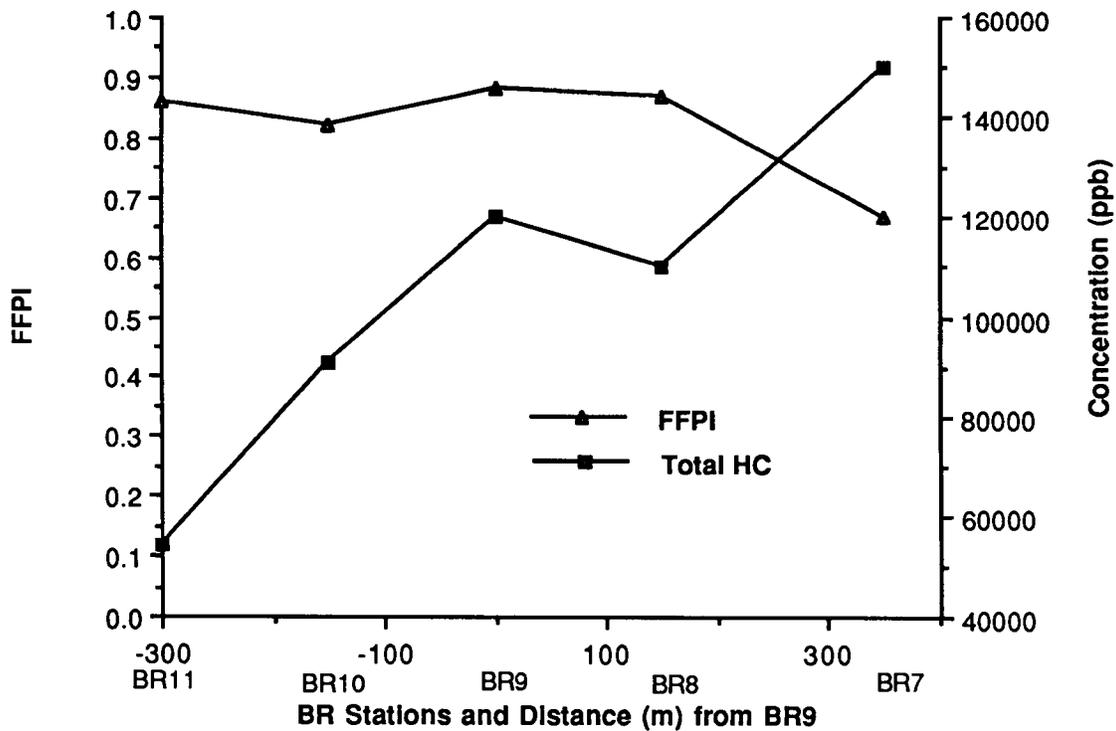
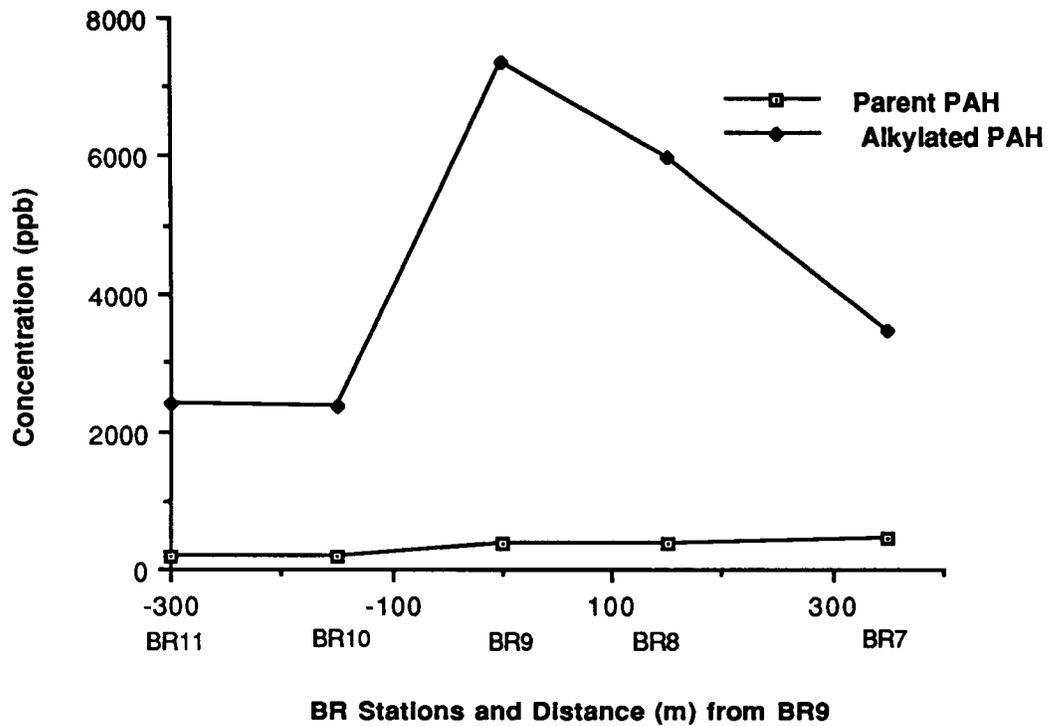


Figure 6.20. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from transect 1, Bayou Rigaud, February 1989.

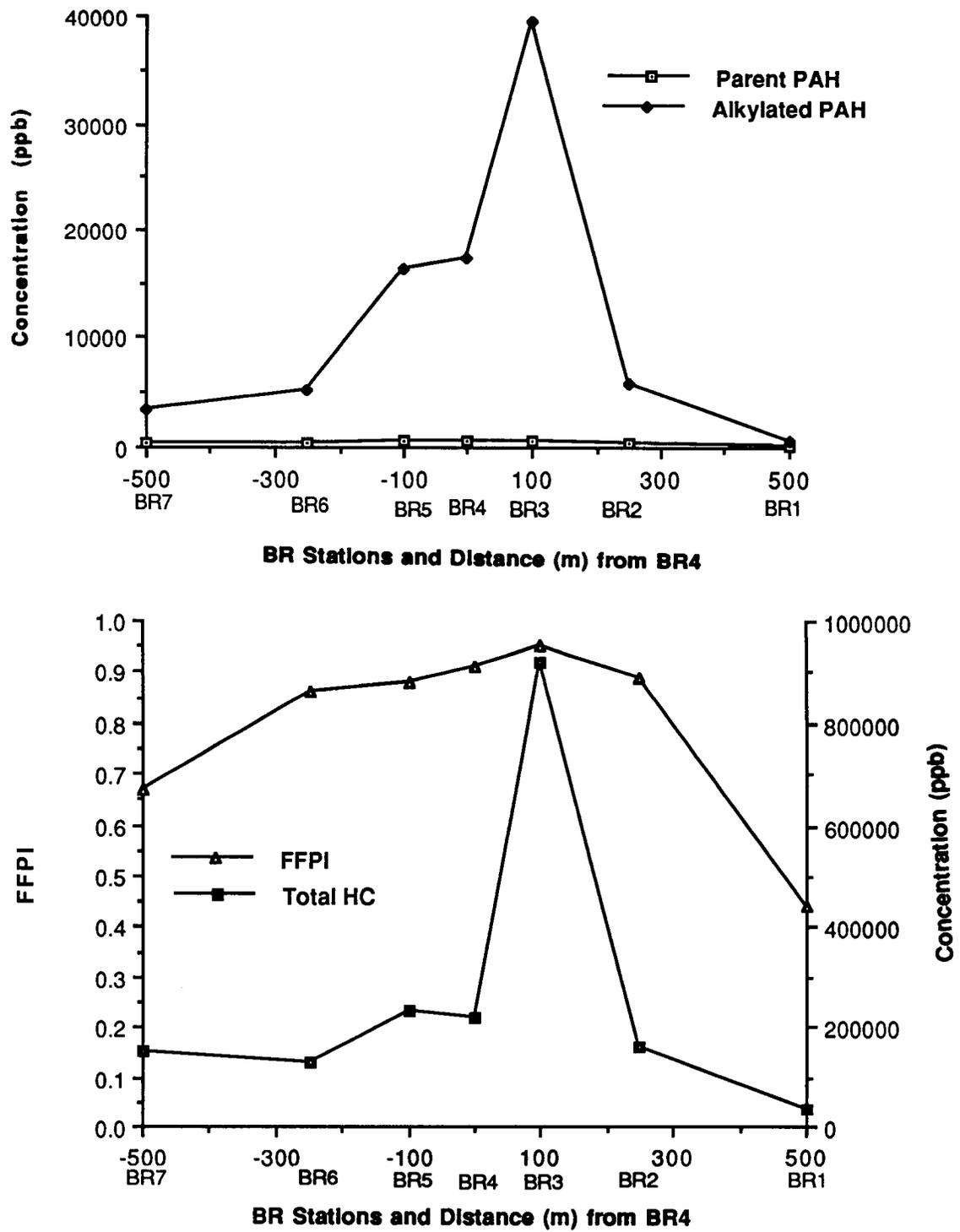


Figure 6.21. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from transect 2, Bayou Rigaud, February 1989.

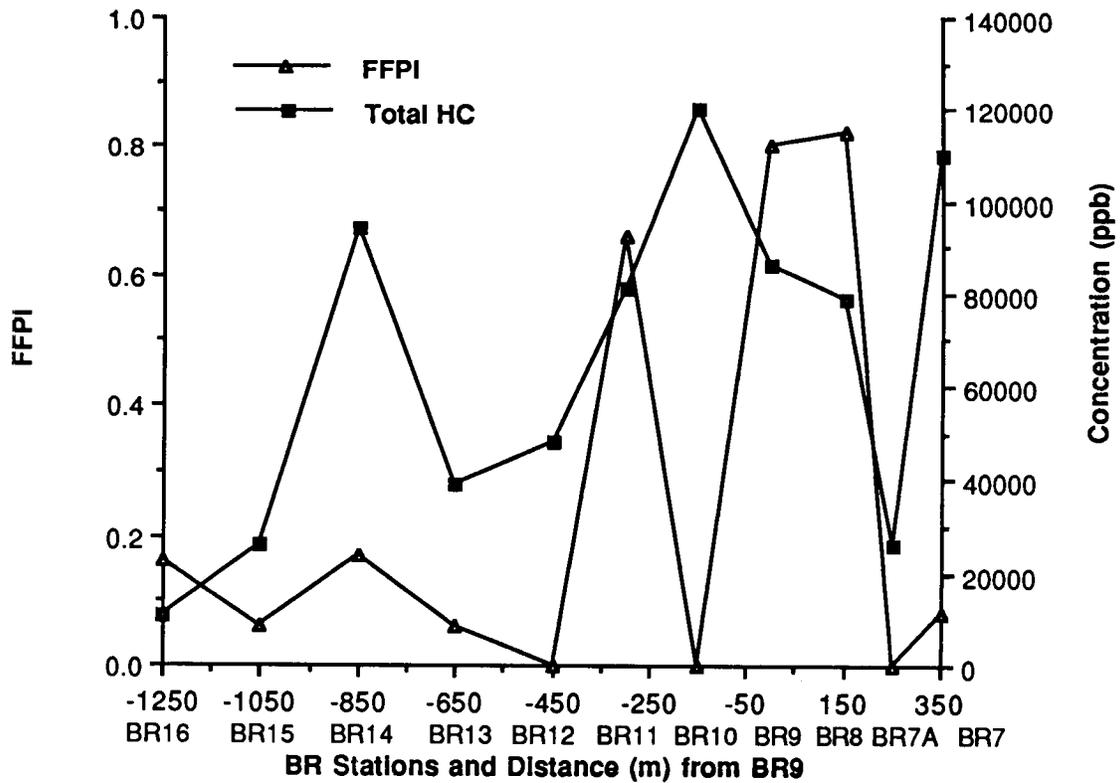
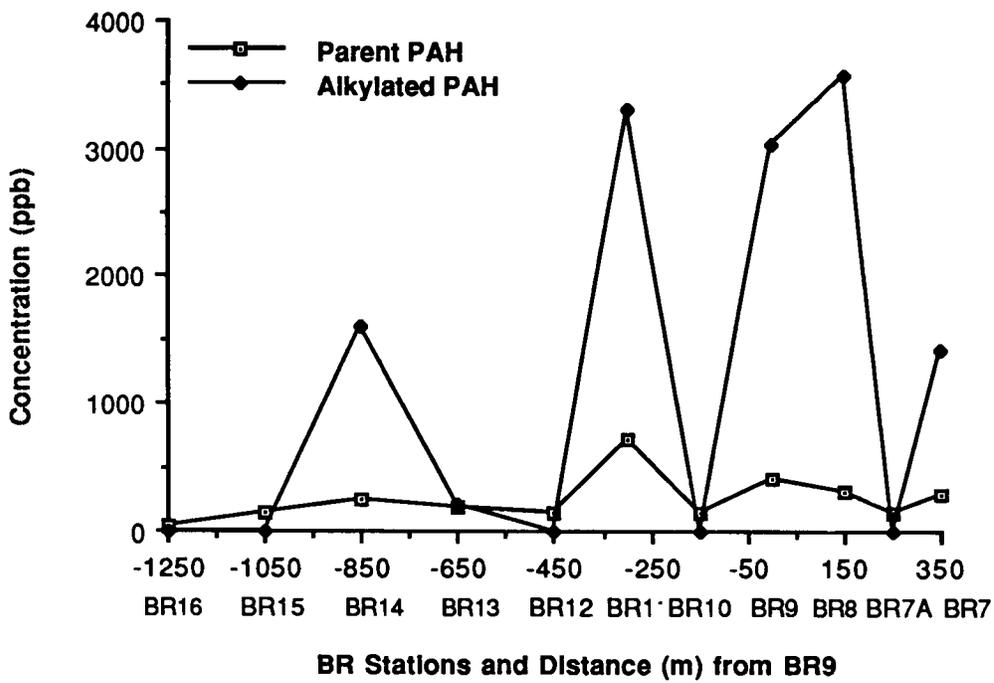


Figure 6.22. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from transect 1, Bayou Rigaud, May 1989.

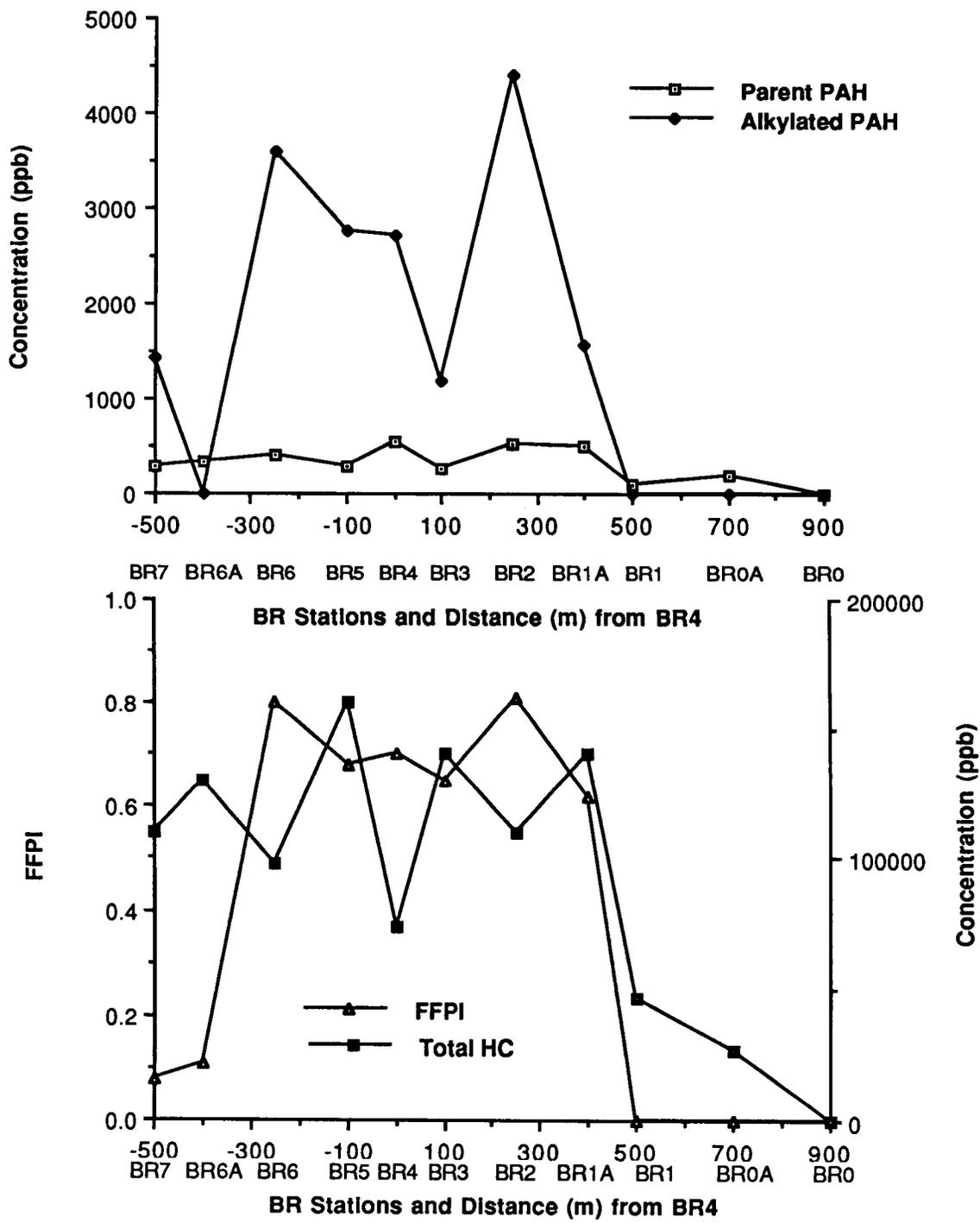


Figure 6.23. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from transect 2, Bayou Rigaud, May 1989.

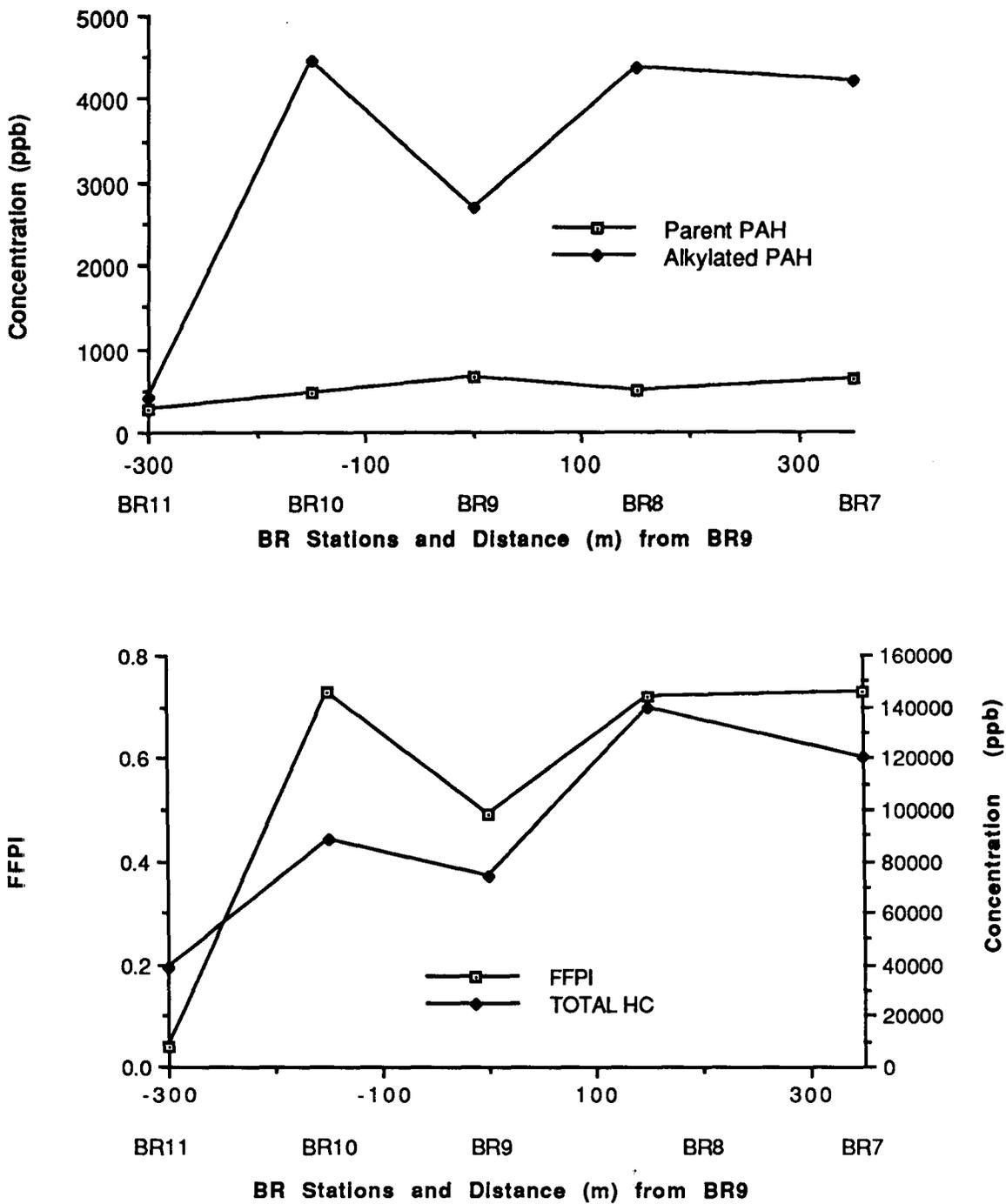


Figure 6.24. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from transect 1, Bayou Rigaud, October 1989.

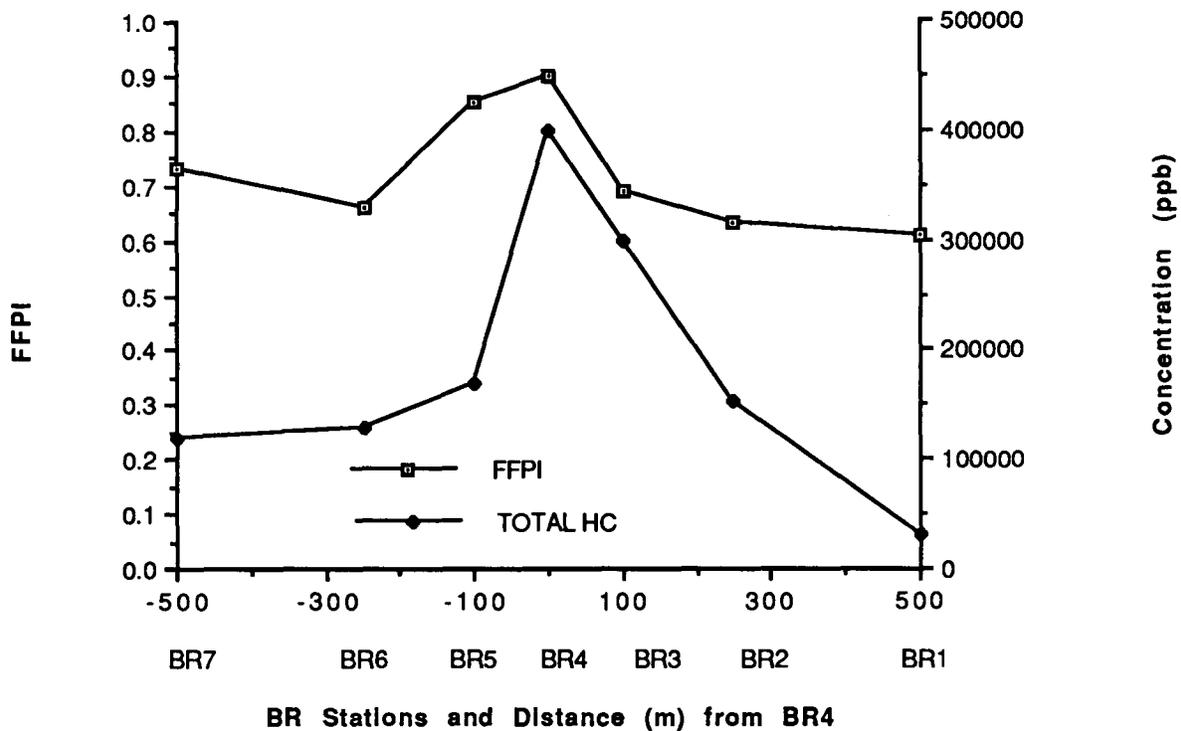
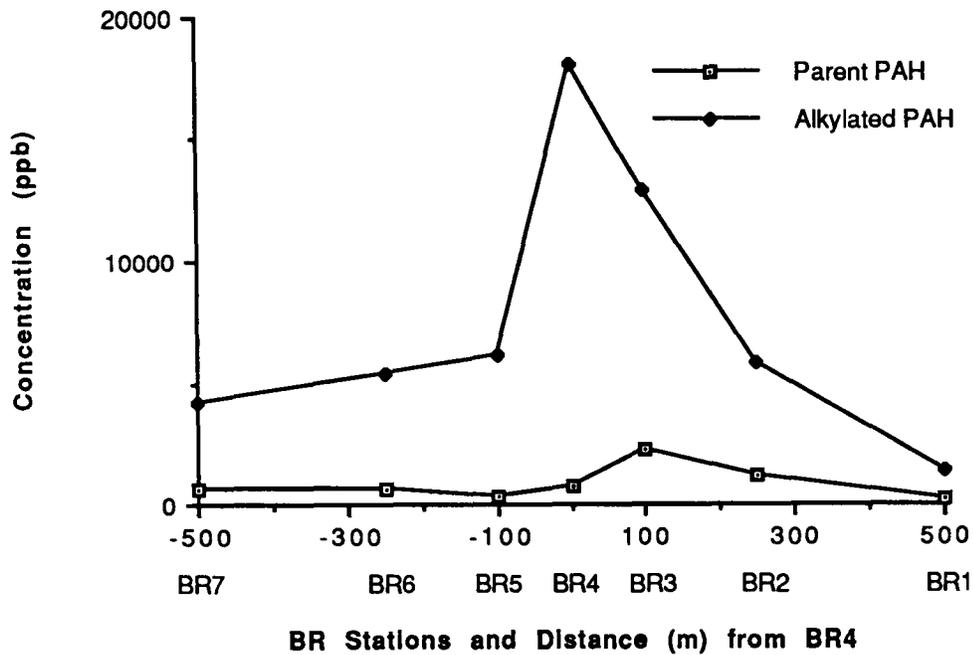


Figure 6.25. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from transect 2, Bayou Rigaud, October 1989.

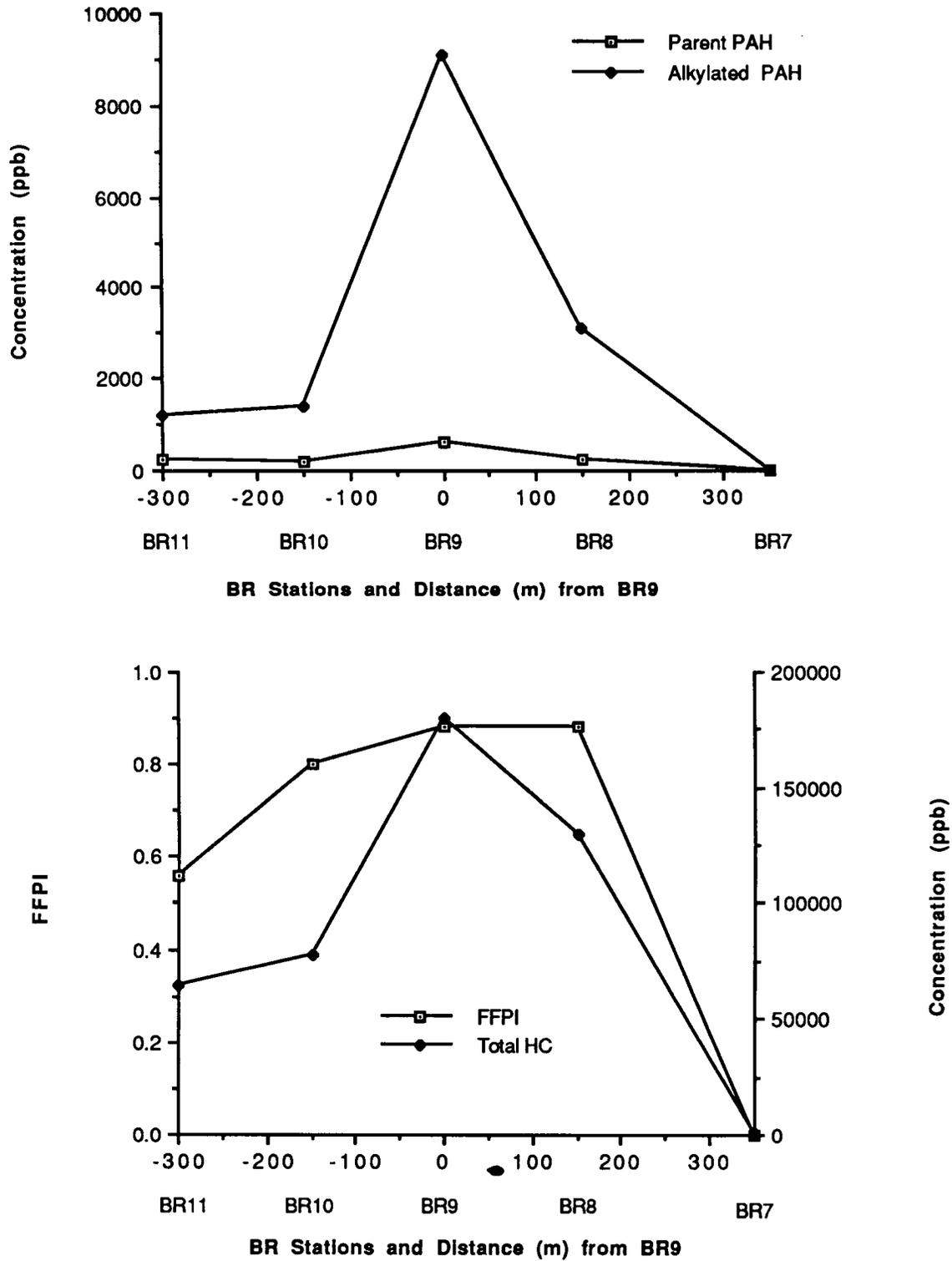


Figure 6.26. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from transect 1, Bayou Rigaud, February 1990.

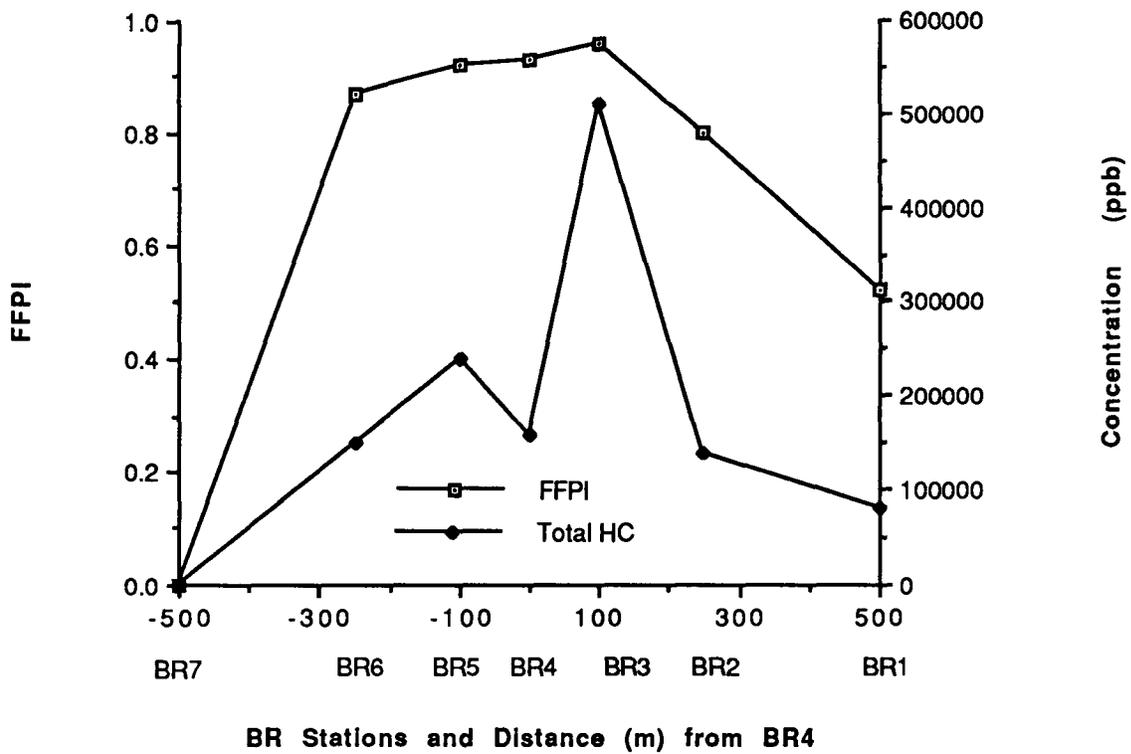
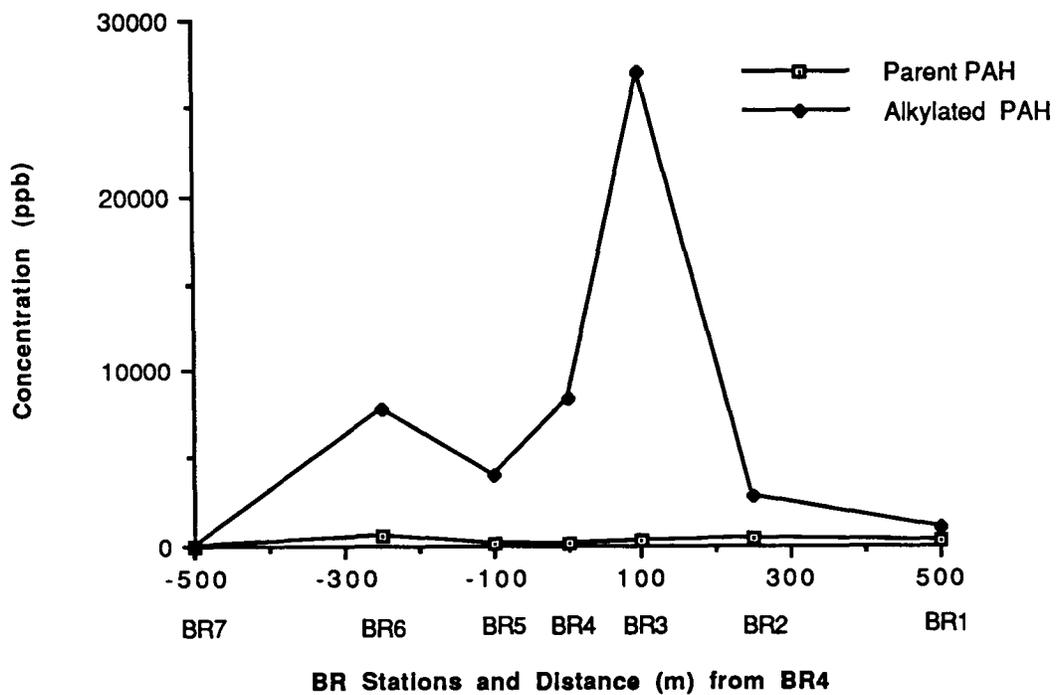


Figure 6.27. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from transect 2, Bayou Rigaud, February 1990.

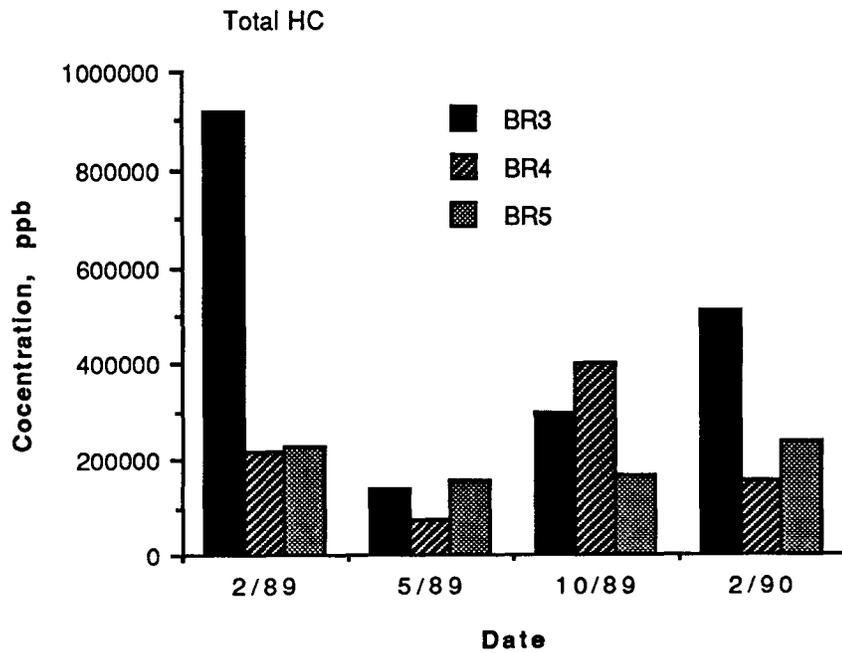
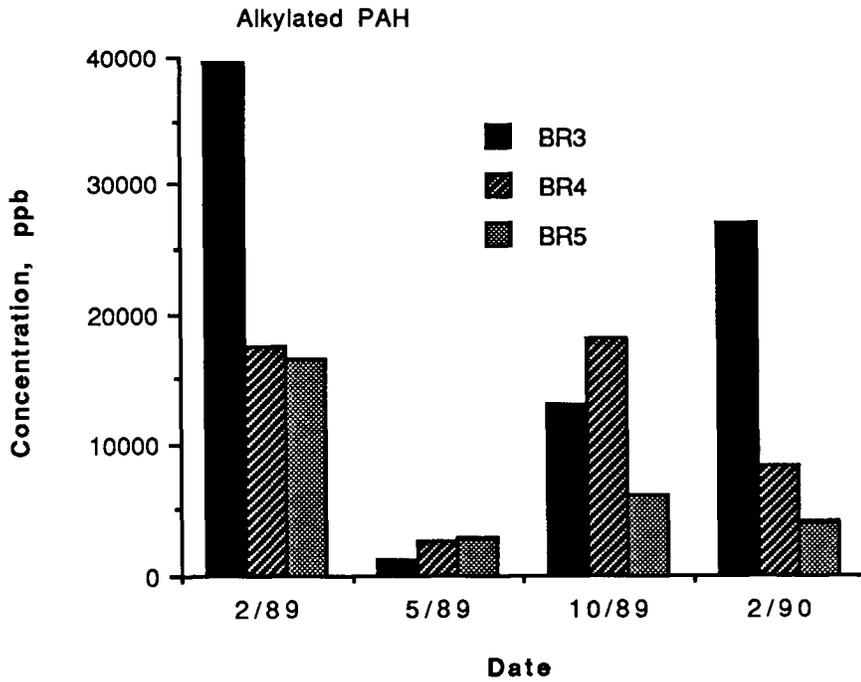


Figure 6.28. Temporal distributions of alkylated PAH and total HC concentrations in surface sediments from selected stations at Bayou Rigaud.

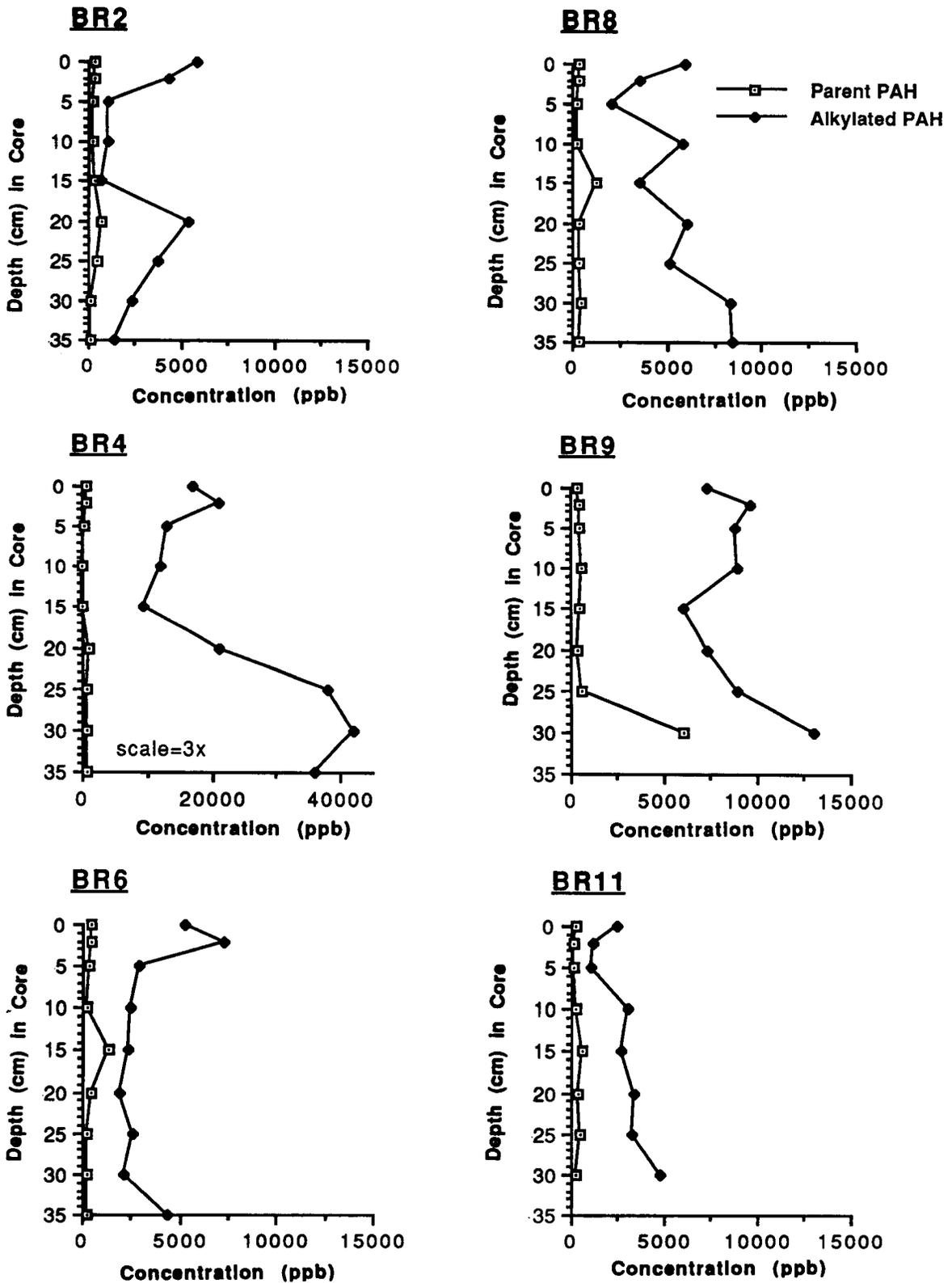


Figure 6.29. Total parent and alkylated PAH concentrations in vertical sediment core sections from Bayou Rigaud, February 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

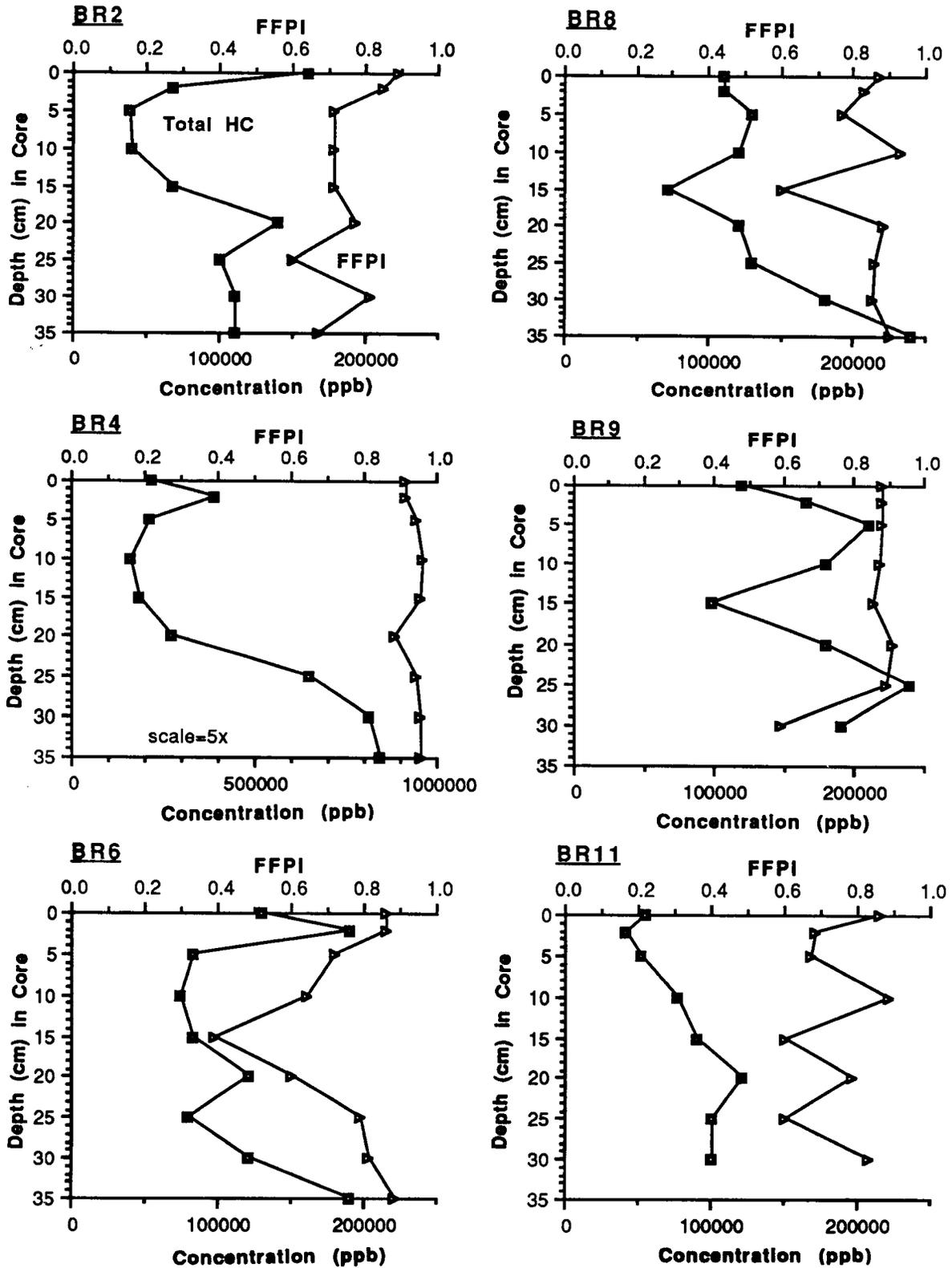


Figure 6.30. FFPI and total HC concentrations in vertical sediment core sections from Bayou Rigaud, February 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

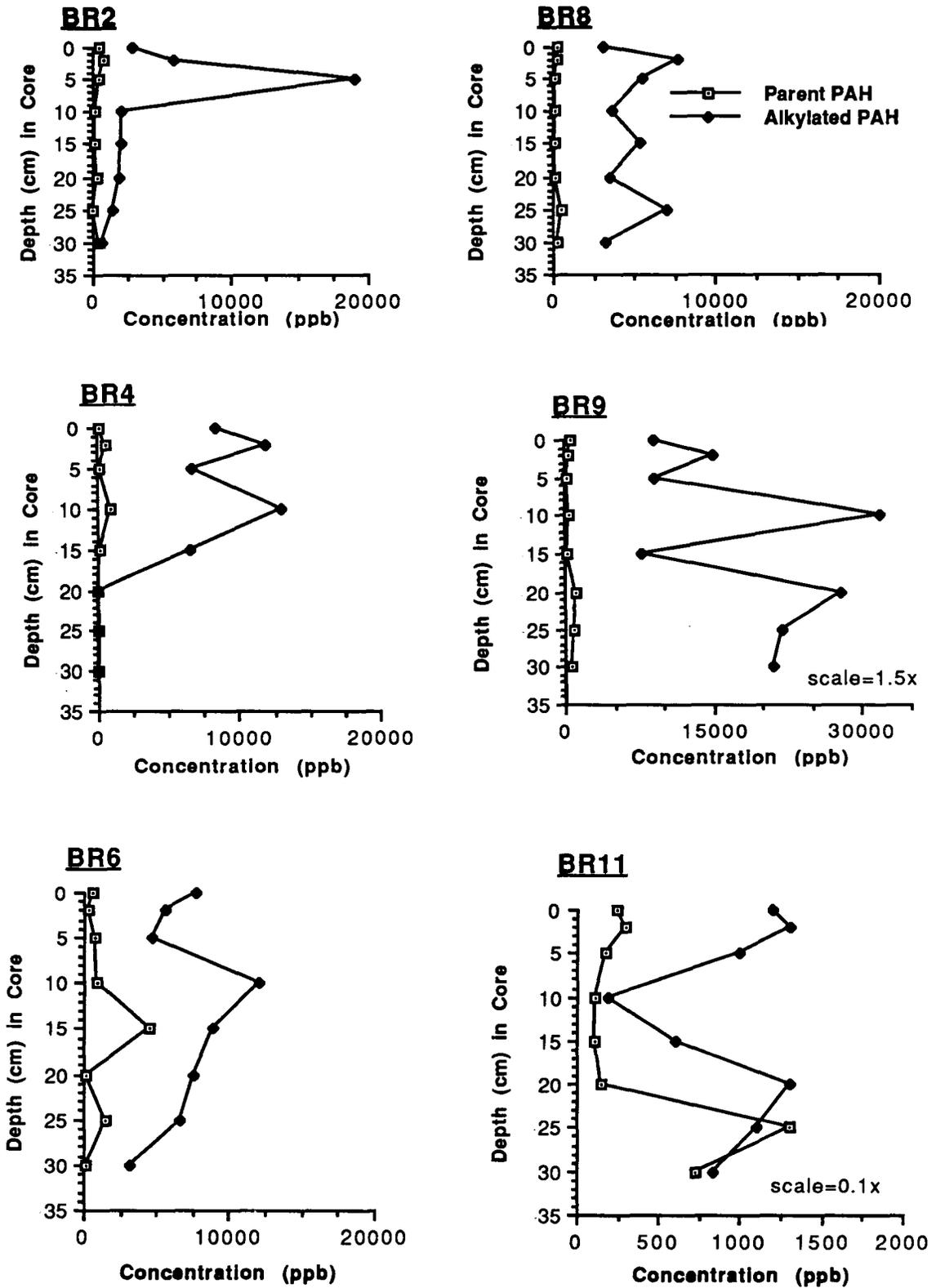


Figure 6.31. Total parent and alkylated PAH concentrations in vertical sediment core sections from Bayou Rigaud, February 1990. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

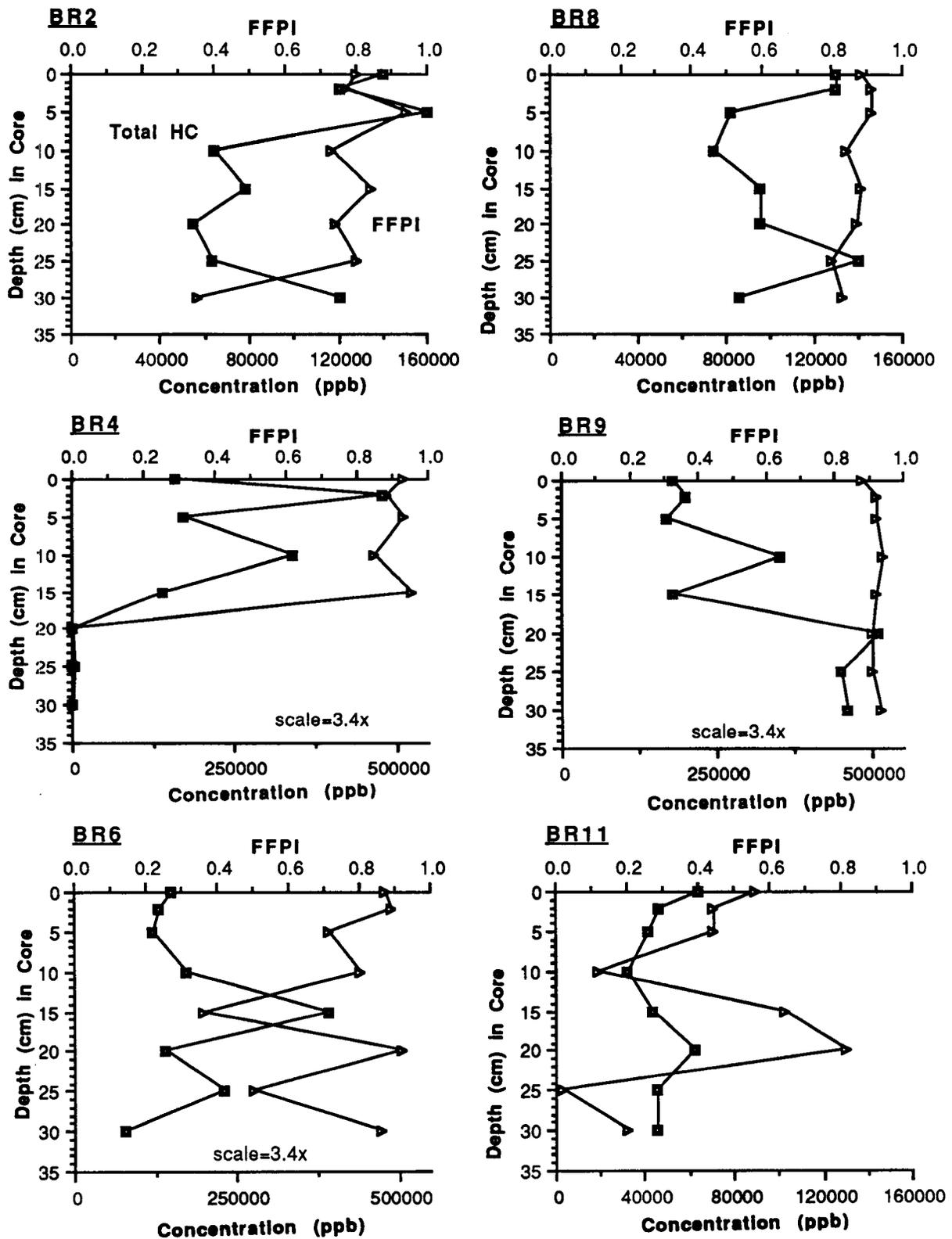


Figure 6.32. FFPI and total HC concentrations in vertical sediment core sections from Bayou Rigaud, February 1990. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

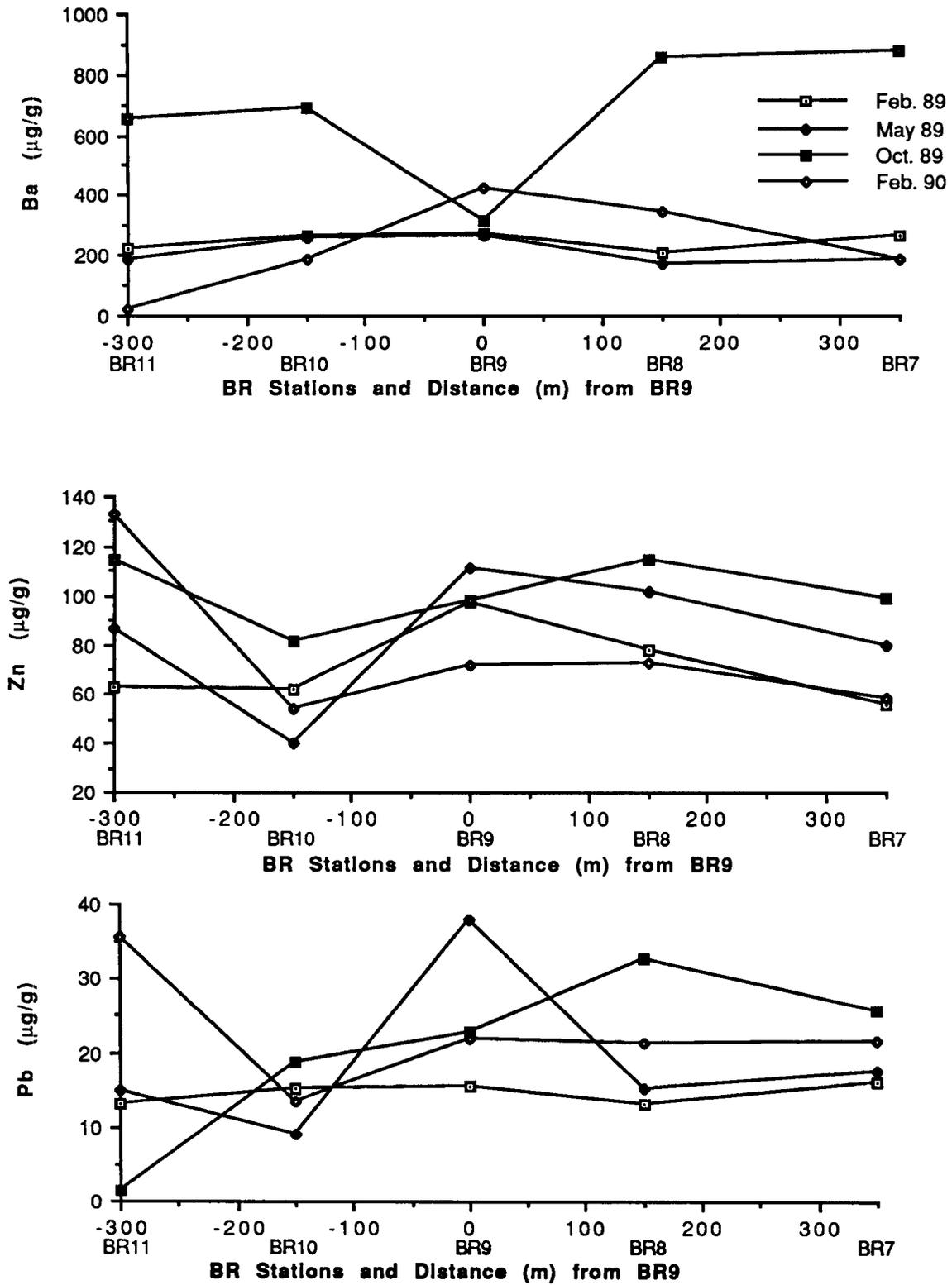


Figure 6.33. Spatial distribution of selected trace metal concentrations in surface sediments from transect 1 in Bayou Rigaud for four sample periods.

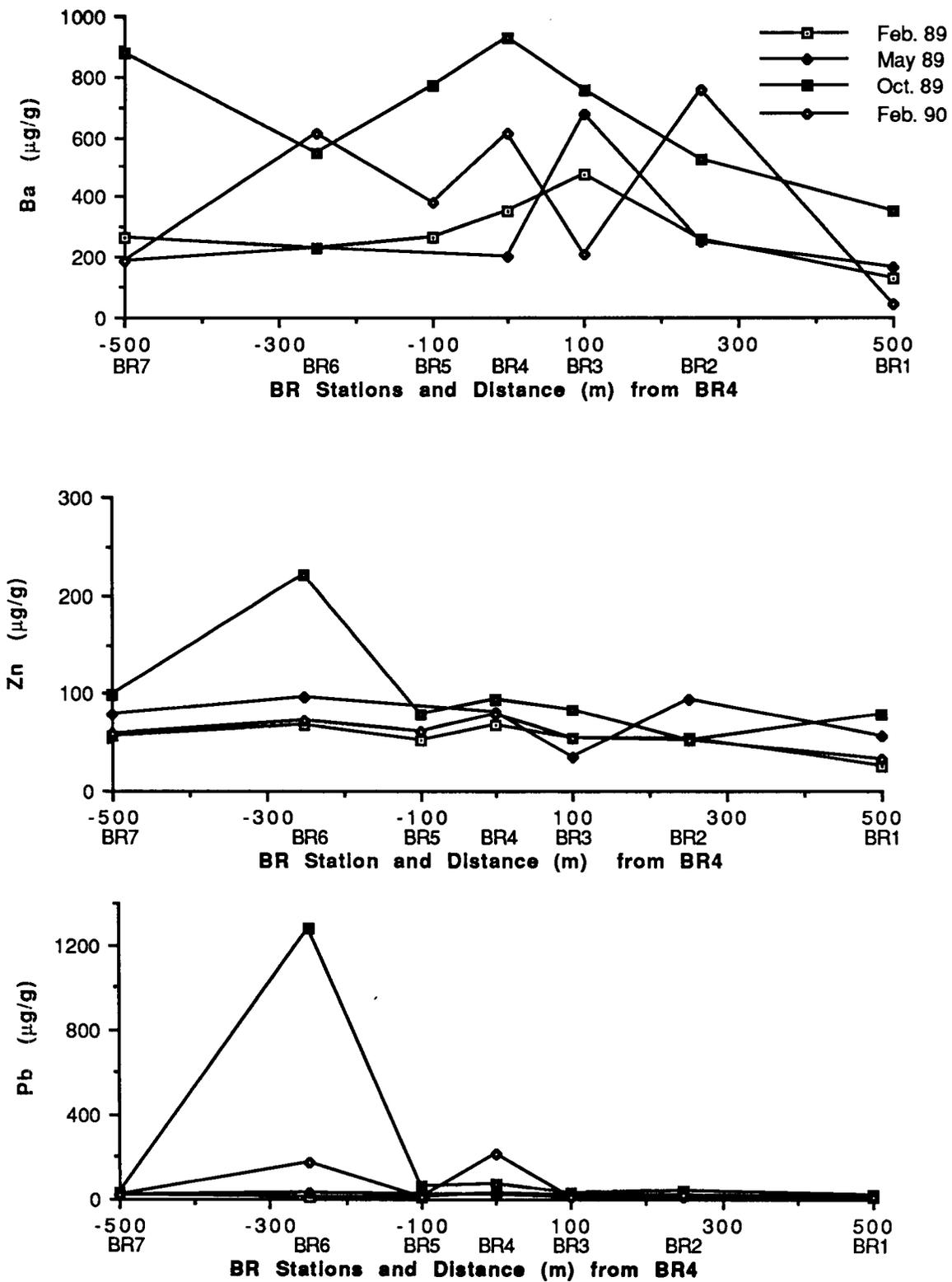


Figure 6.34. Spatial distribution of selected trace metal concentrations in surface sediments from transect 2 in Bayou Rigaud for four sample periods.

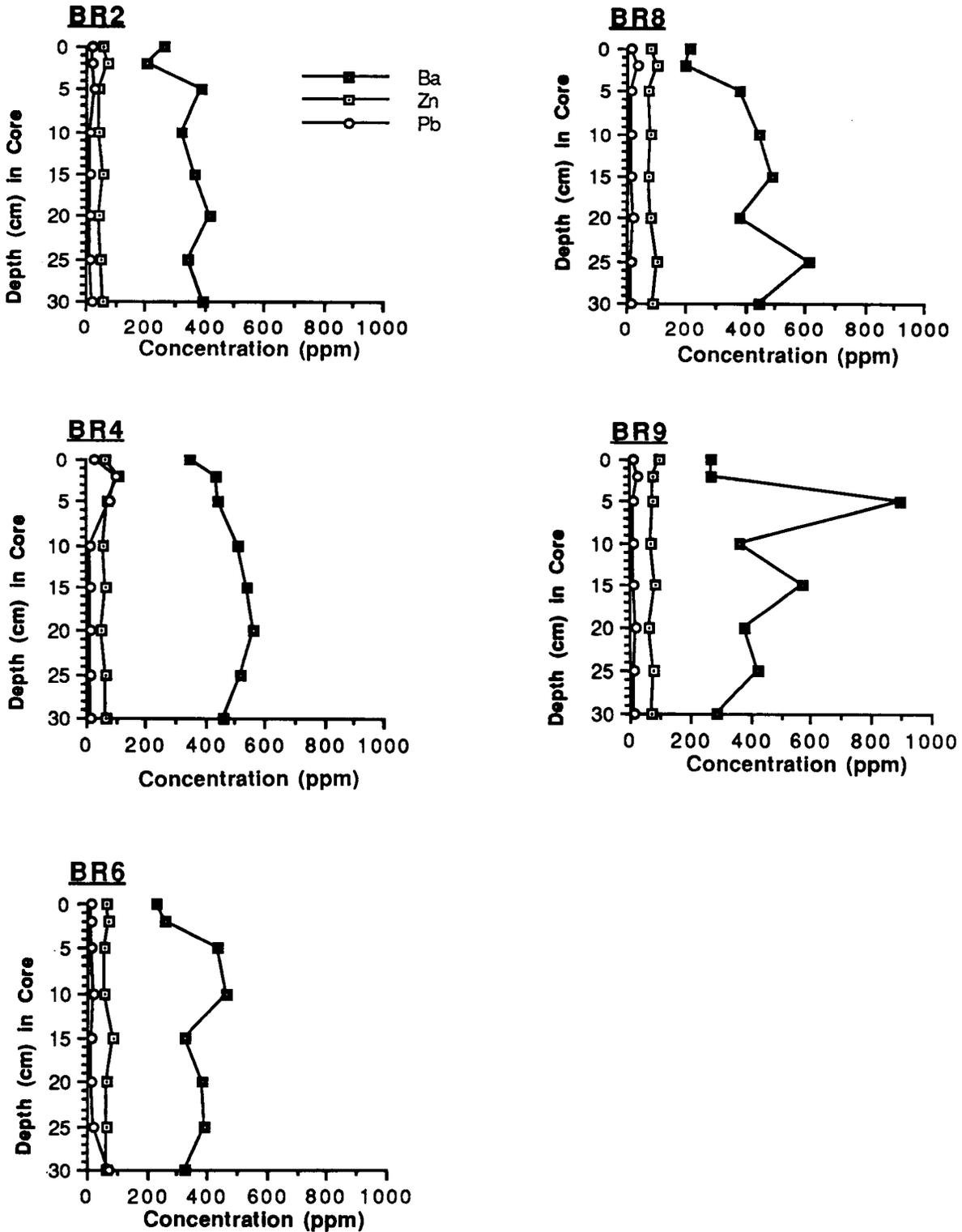


Figure 6.35. Selected trace metal concentrations in vertical sediment core sections from selected stations in Bayou Rigaud, February 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

BAYOU RIGAUD: FEBRUARY 1989 SURFACE SEDIMENT Pb-210

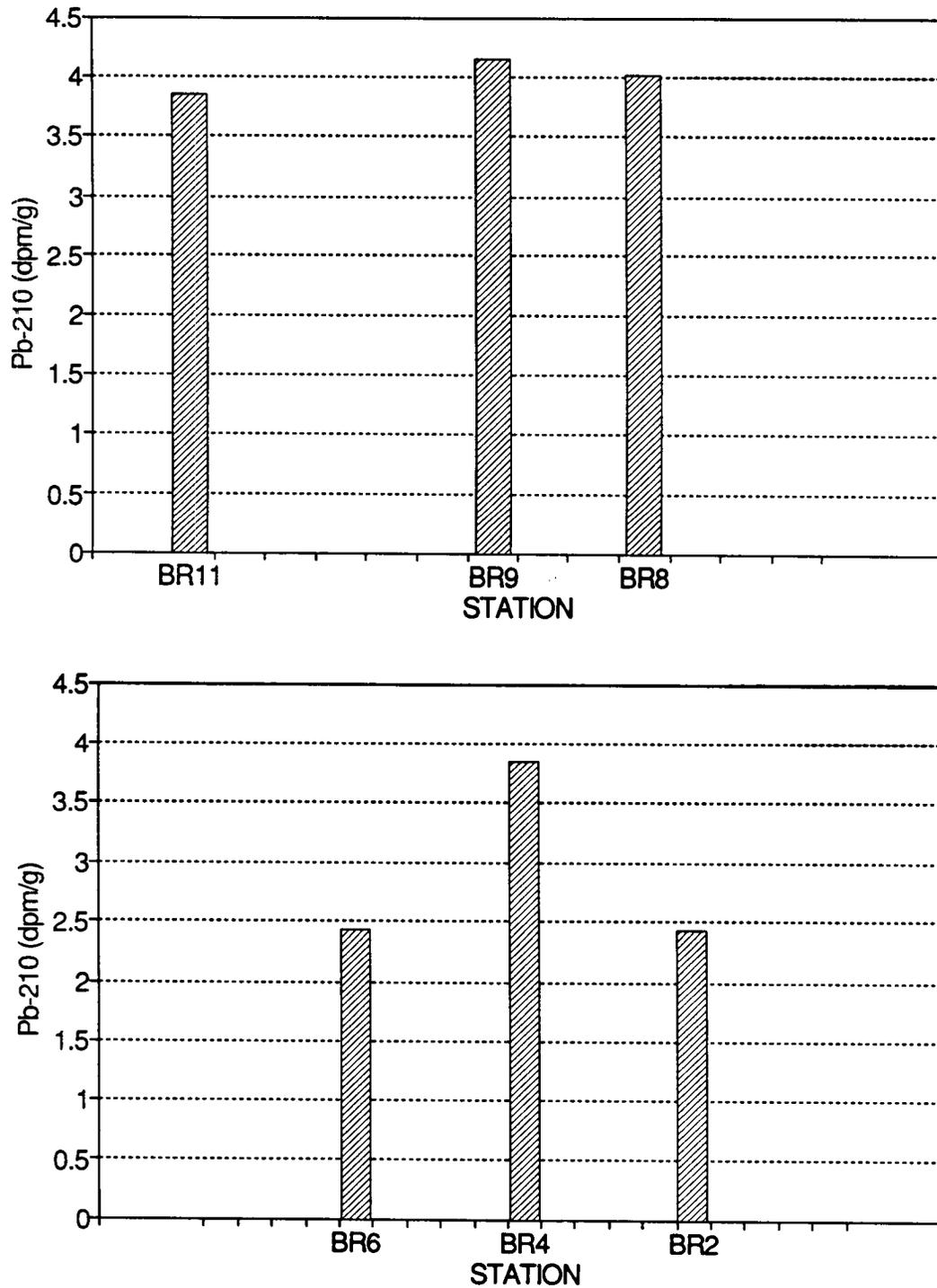


Figure 6.36. Spatial distribution of Pb-210 activities in surface sediments from Bayou Rigaud, February 1989.

BAYOU RIGAUD: MAY 1989 SURFACE SEDIMENT Pb-210

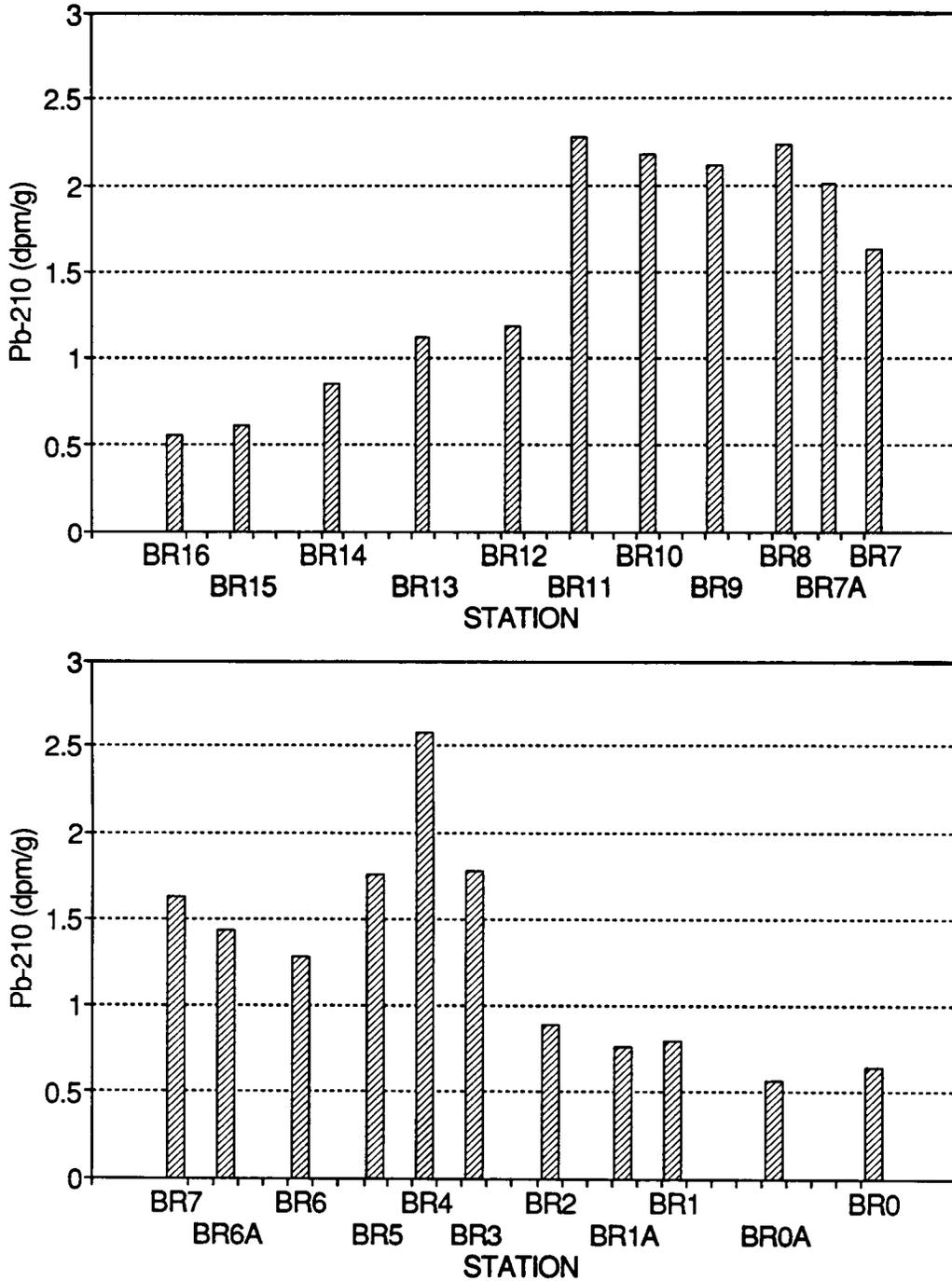


Figure 6.37. Spatial distribution of Pb-210 activities in surface sediments from Bayou Rigaud, May 1989.

BAYOU RIGAUD: OCTOBER 1989 SURFACE SEDIMENT Pb-210

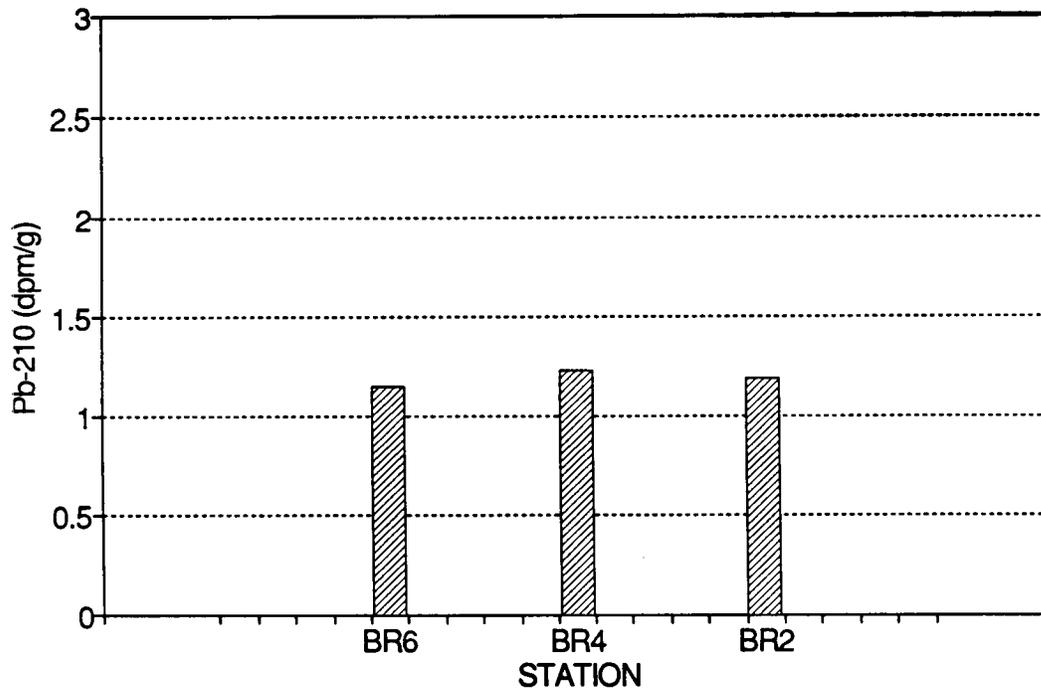
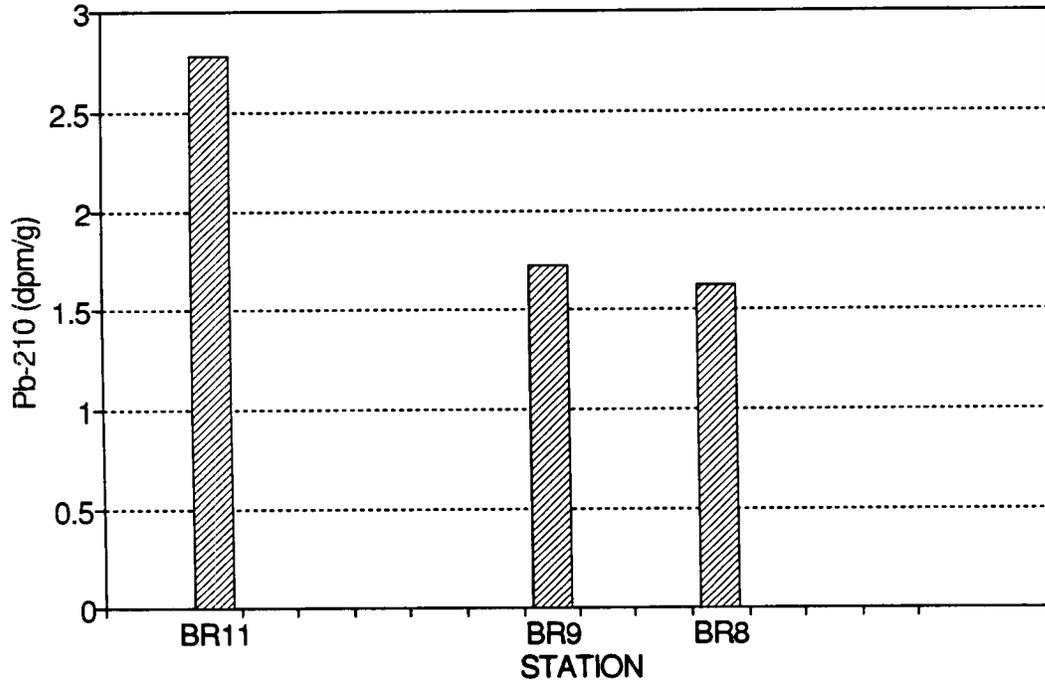


Figure 6.38. Spatial distribution of Pb-210 activities in surface sediments from Bayou Rigaud, October 1989.

BAYOU RIGAUD: FEBRUARY 1990 SURFACE SEDIMENT Pb-210

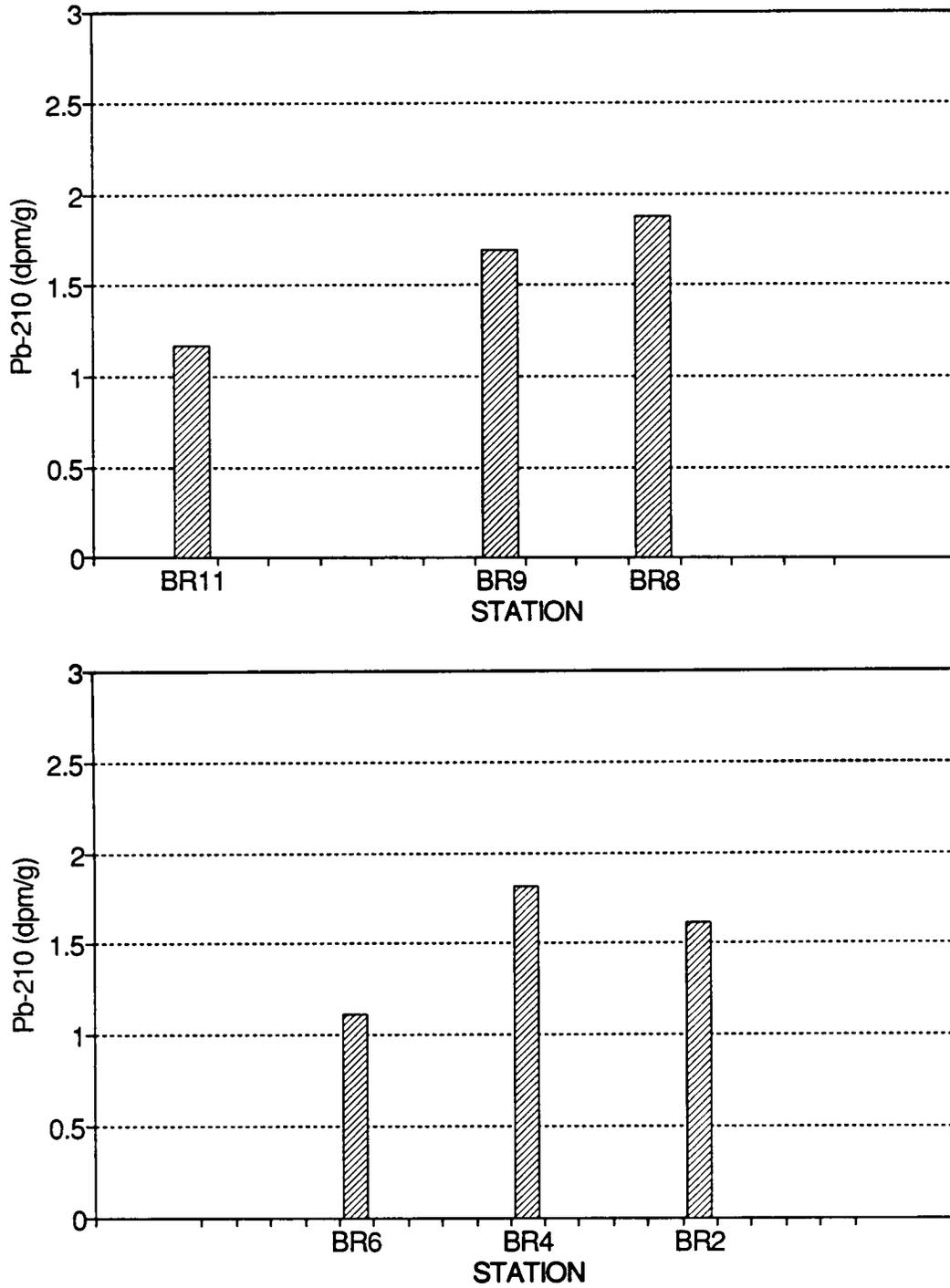


Figure 6.39. Spatial distribution of Pb-210 activities in surface sediments from Bayou Rigaud, February 1990.

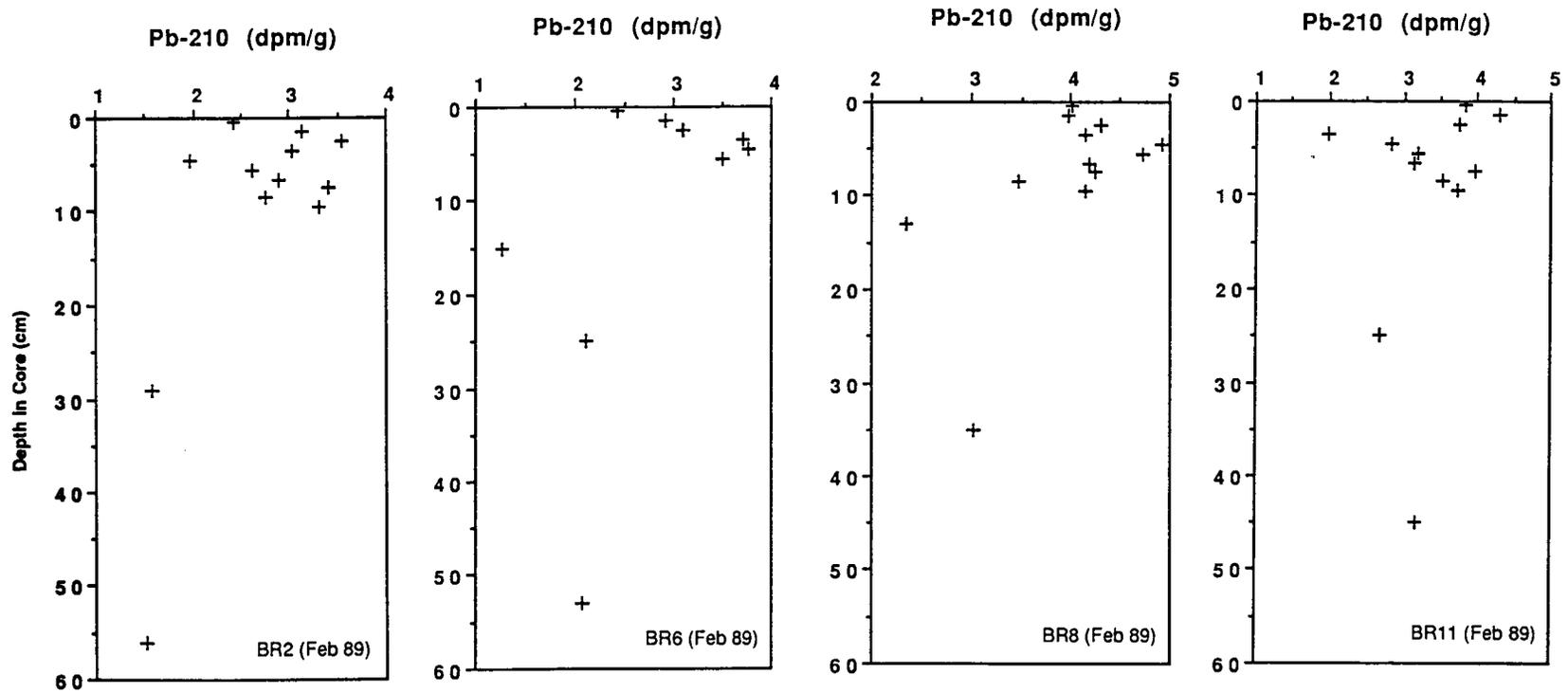


Figure 6.40. Pb-210 activities in vertical sediment core sections from selected stations in Bayou Rigaud, February 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

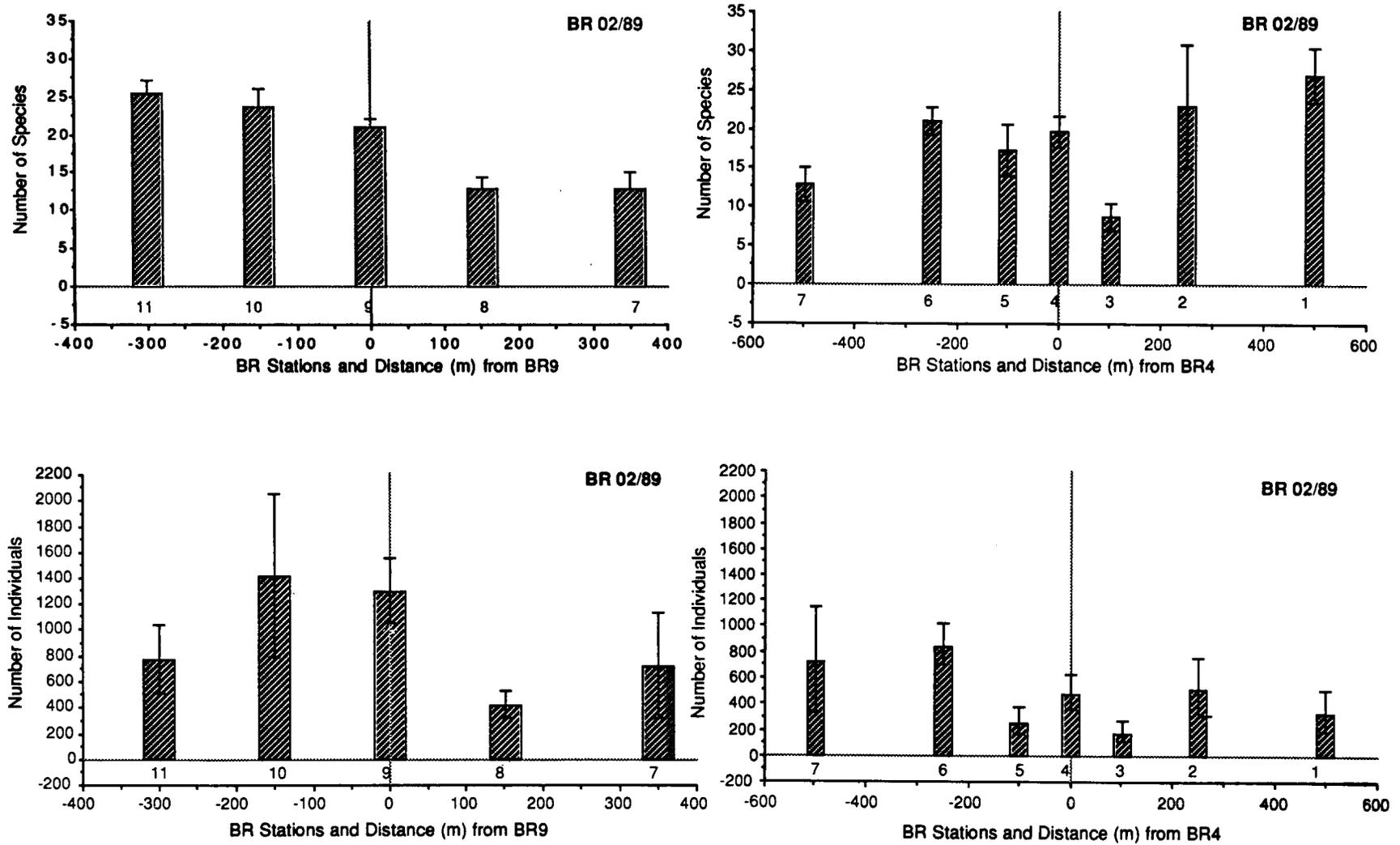


Figure 6.41. Spatial distribution of number of species per replicate (mean \pm standard error) and number of individuals per replicate (mean \pm standard error) for Bayou Rigaud, February 1989.

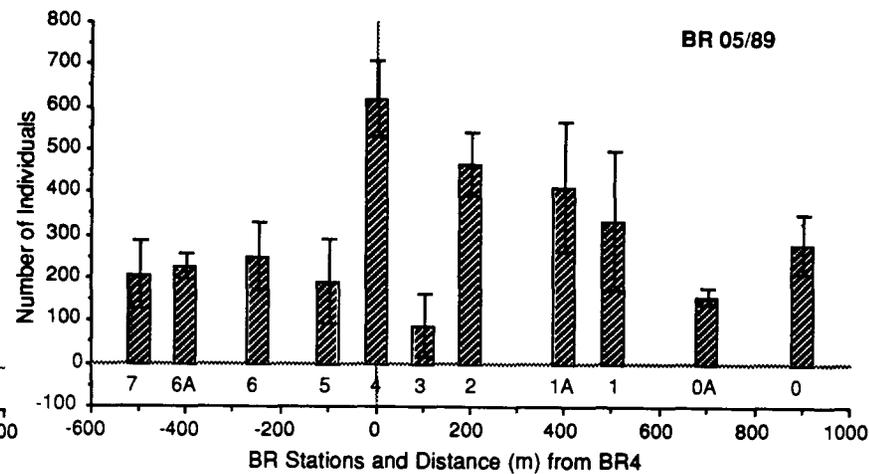
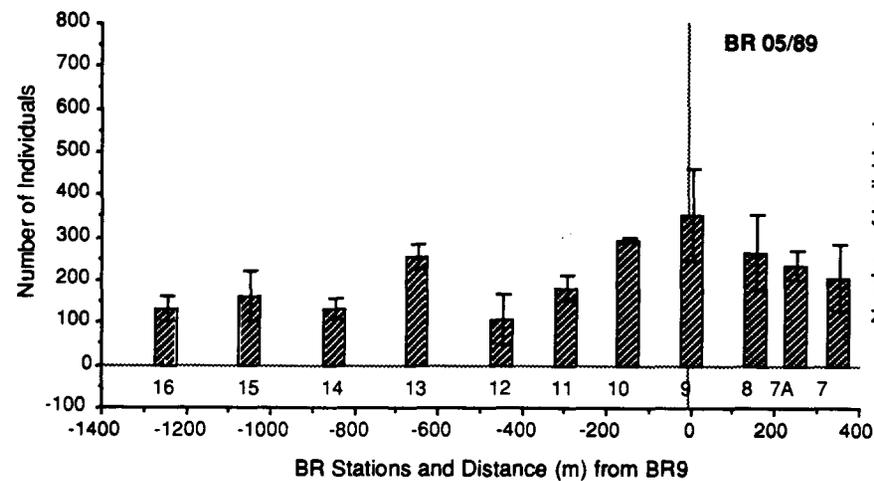
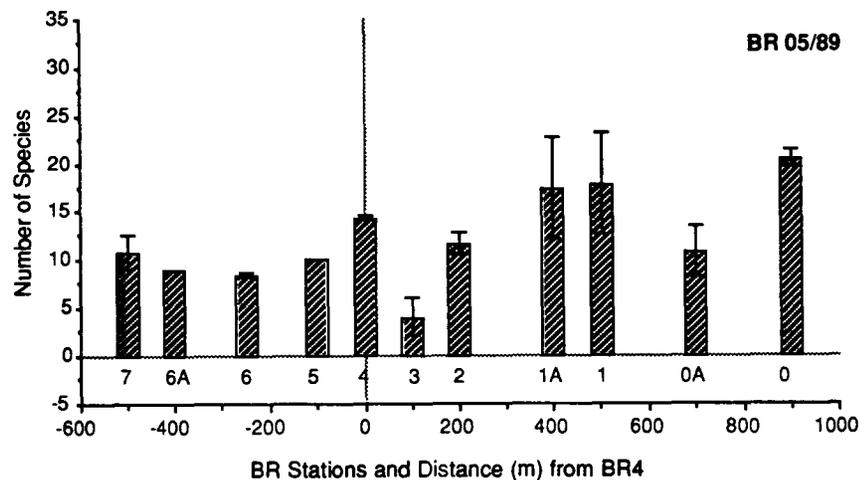
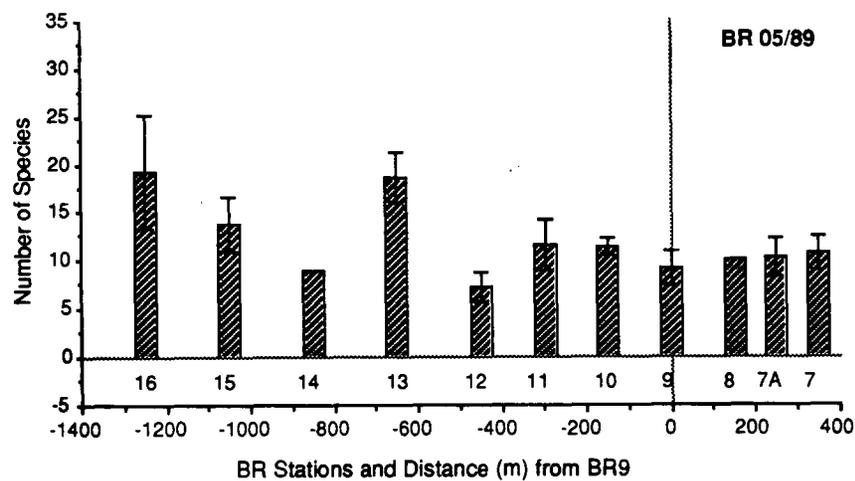


Figure 6.42. Spatial distribution of number of species per replicate (mean ± standard error) and number of individuals per replicate (mean ± standard error) for Bayou Rigaud, May 1989.

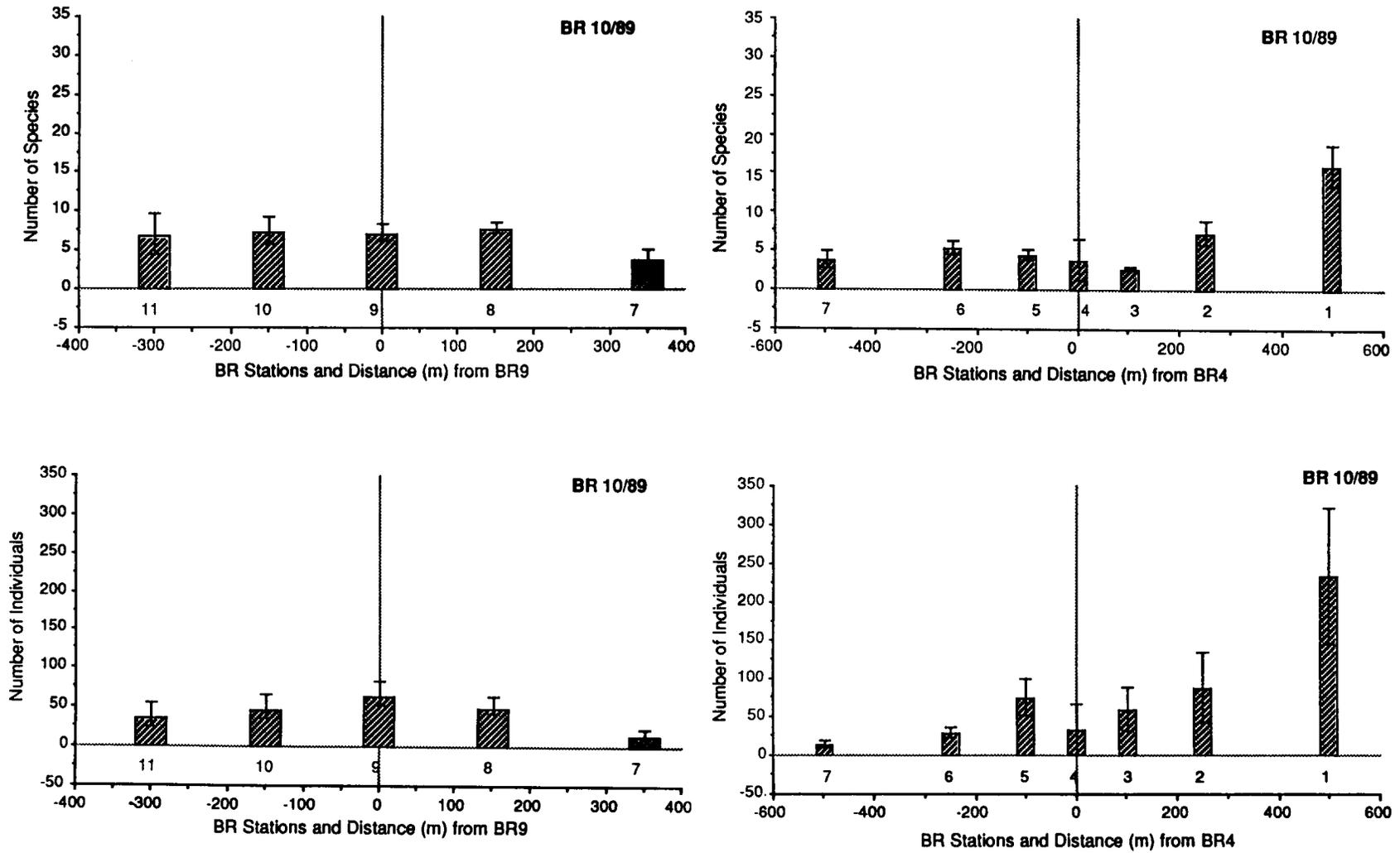


Figure 6.43. Spatial distribution of number of species per replicate (mean \pm standard error) and number of individuals per replicate (mean \pm standard error) for Bayou Rigaud, October 1989.

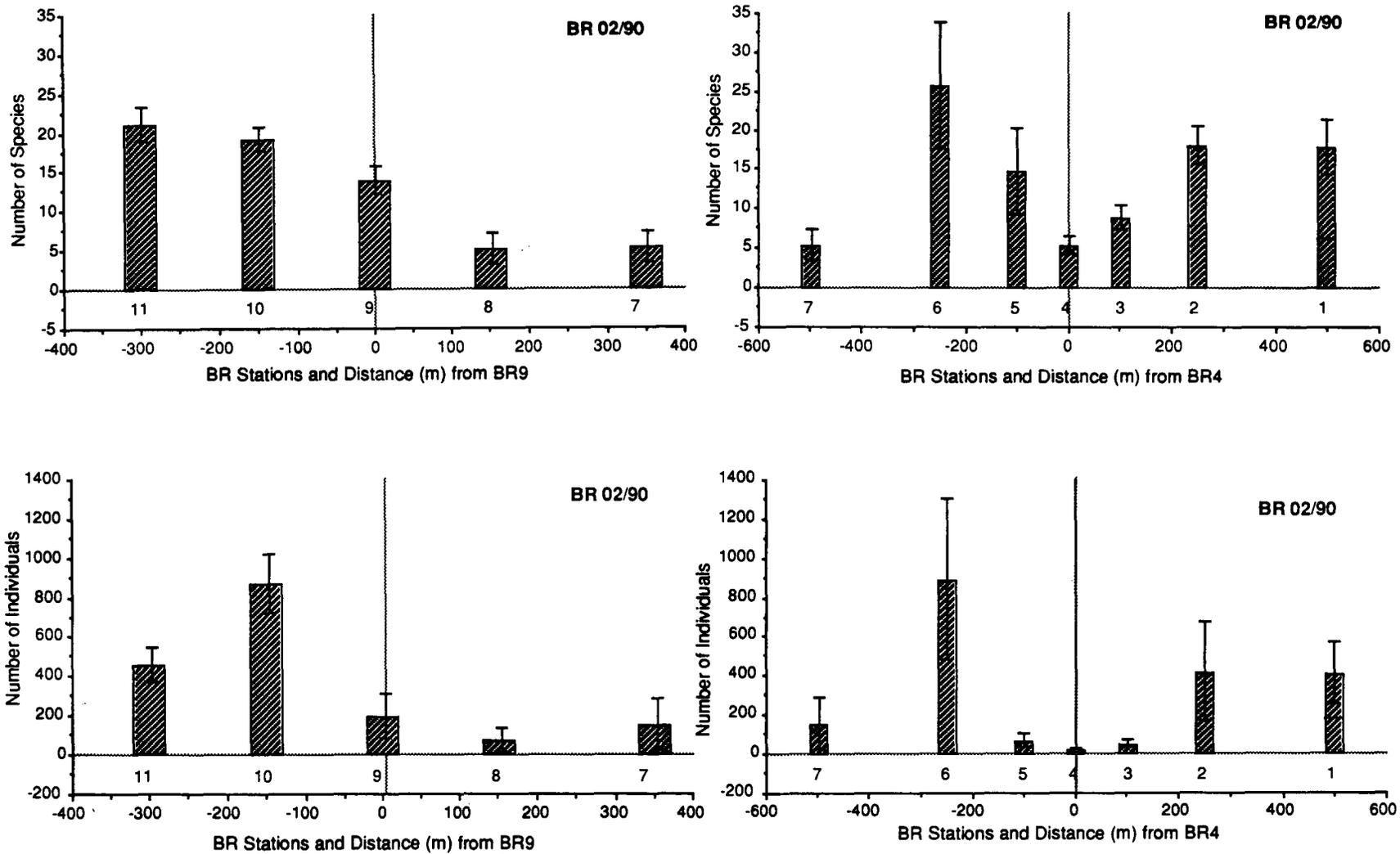


Figure 6.44. Spatial distribution of number of species per replicate (mean \pm standard error) and number of individuals per replicate (mean \pm standard error) for Bayou Rigaud, February 1990.

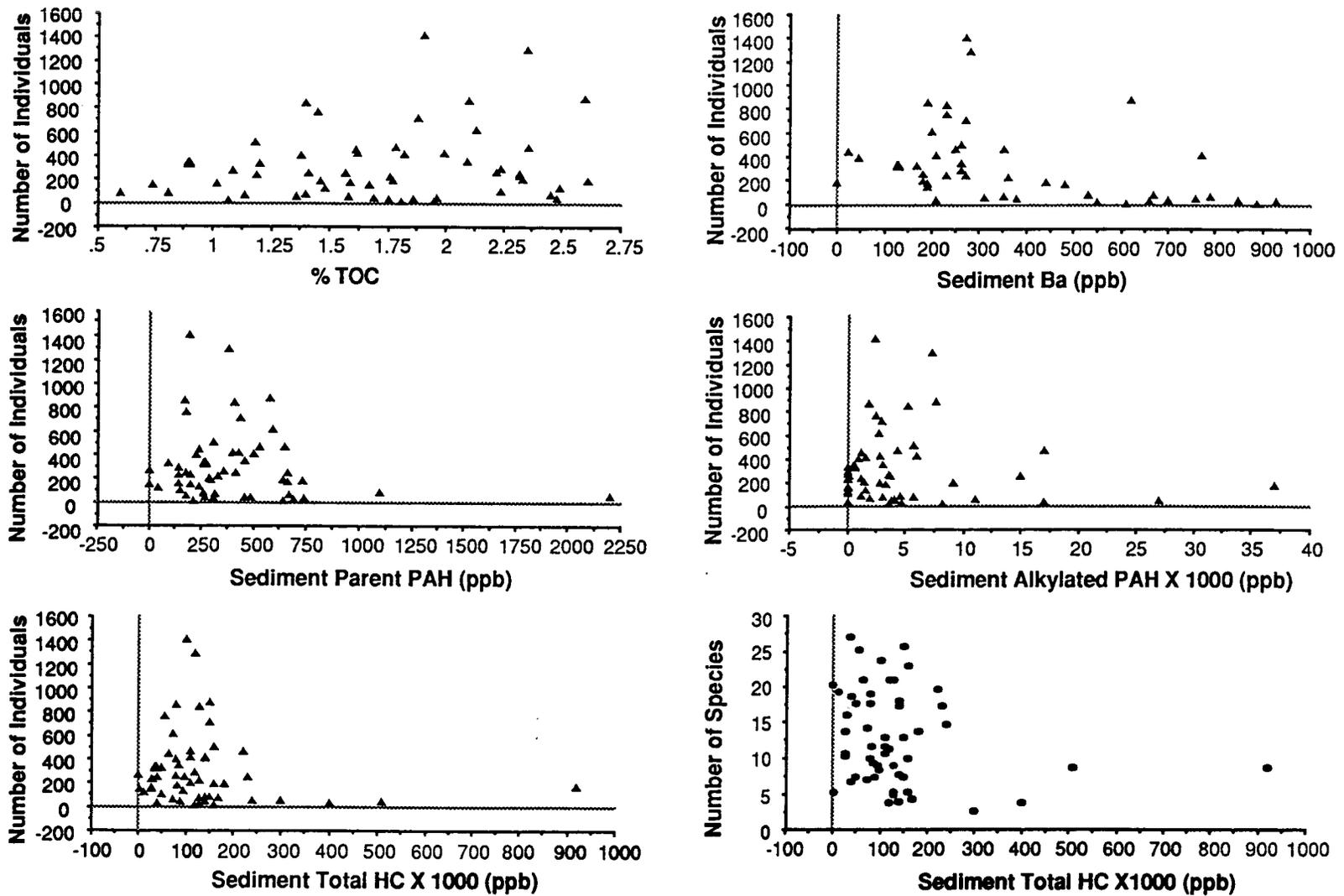


Figure 6.45. Relationship of mean number of species per replicate and mean number of individuals per replicate to various sediment characteristics for Bayou Rigaud for all sample periods combined.

Table 6.1. Comparison of average daily discharges ($\text{bbl}\cdot\text{d}^{-1}$) and oil and grease content ($\text{mg}\cdot\text{l}^{-1}$) of produced waters from facilities at Bayou Rigaud study area. (Data provided by operators.)

Date	Facility	
	Conoco	Exxon
02/89 Discharge	96,531	40,100
Oil and Grease	20	38
05/89 Discharge	91,198	39,000
Oil and Grease	29	24
11/89 Discharge	110,500	39,200
Oil and Grease	16	32
02/90 Discharge	107,082	39,100
Oil and Grease	17	49
Average Discharge	105,760*	40,000*
Average Oil and Grease	19*	41*

*Mean of 25 monthly sample dates from 02/88 - 02/90.

Table 6.2. Duncan's multiple range test for Bayou Rigaud study area, February 1989; underlined stations are not significantly different from each other.

Number of Species (square root transformed):

1	11	10	2	9	6	4	5	8	7	3
---	----	----	---	---	---	---	---	---	---	---

Diversity (H'):

1	11	2	4	5	6	3	10	8	9	7
---	----	---	---	---	---	---	----	---	---	---

Evenness (J'):

1	11	2	3	5	4	6	8	10	9	7
---	----	---	---	---	---	---	---	----	---	---

Table 6.3. Duncan's multiple range test for Bayou Rigaud study area, May 1989; underlined stations are not significantly different from each other.

Number of Species (square root transformed):

0	13	16	1	1A	4	15	2	11	10	7	0A	7A	5	8	9	6A	14	6	12	3
_____										_____										
_____										_____										

Number of Individuals (natural log transformed):

4	2	1A	9	10	0	13	8	6	7A	1	6A	7	11	0A	5	15	14	16	12	3
_____										_____										
_____										_____										

Diversity (H')

160	15	13	1	1A	11	0A	14	12	7	5	10	8	7A	6	6A	2	4	9	3
_____										_____									
_____										_____									

Evenness (J')

16	15	0	14	0A	11	12	1	3	1A	13	7	5	8	10	7A	6	6A	2	4	9
_____										_____										
_____										_____										
_____										_____										

Table 6.4. Duncan's multiple range test for Bayou Rigaud study area, October 1989; underlined.

Number of Species (square root transformed):

1 8 2 10 9 11 6 5 7 3 4

Number of Individuals (natural log transformed):

1 2 5 9 3 8 10 6 11 7 4

Diversity (H'):

1 11 10 8 9 6 7 2 4 5 3

* Evenness (J'):

11 10 7 1 8 4 6 9 5 2 3

* Cell sizes unequal due to missing values.

Table 6.5. Duncan's multiple range test for Bayou Rigaud study area, February 1990; underlined stations are not significantly different from each other.

Number of Species (square root transformed):										
6	11	10	2	1	5	9	3	4	7	8
<hr/>							<hr/>			
Number of Individuals (natural log transformed):										
10	6	11	1	2	9	7	5	3	8	4
<hr/>					<hr/>					
Diversity (H')										
5	3	9	2	4	11	6	10	1	8	7
<hr/>		<hr/>							<hr/>	
Evenness (J')										
5	4	3	9	2	8	11	7	6	10	1
<hr/>			<hr/>							

Table 6.6. Duncan's multiple range test for Bayou Rigaud study area, all sample periods combined for 11 stations; underlined stations or dates are not significantly different from each other.

Number of Species (square root transformed):

1	11	10	2	6	9	5	4	8	7	3
		<u>2/89</u>		<u>02/90</u>		<u>05/89</u>		<u>10/89</u>		

Number of Individuals (natural log transformed):

10	1	2	9	6	11	8	5	7	4	3
		<u>2/89</u>		<u>05/89</u>		<u>02/90</u>		<u>10/89</u>		

* Diversity (H'):

11	1	5	10	2	4	6	9	8	3	7
		<u>2/90</u>		<u>02/89</u>		<u>10/89</u>		<u>05/89</u>		

* Evenness (J'):

11	5	1	4	3	8	10	7	6	2	9
		<u>10/89</u>		<u>02/90</u>		<u>05/89</u>		<u>02/89</u>		

* Cell sizes unequal due to missing values.

Table 6.7. Threshold concentrations of various chemical constituents in surficial sediments at Bayou Rigaud at or above which there was a depressed benthic fauna (N/A = not applicable).

Chemical Constituent	Number of Species	Number of Individuals
Surficial Sediments:		
Parent PAH ($\mu\text{g}\cdot\text{g}^{-1}$)	N/A	740
Alkylated PAH ($\mu\text{g}\cdot\text{g}^{-1}$)	N/A	7,700
Total PAH ($\mu\text{g}\cdot\text{g}^{-1}$)	N/A	9,700
Total Saturated HC ($\mu\text{g}\cdot\text{g}^{-1}$)	300,000	240,000
Barium ($\mu\text{g}\cdot\text{g}^{-1}$)	N/A	440

Chapter 7

EMELINE PASS STUDY AREA

7.1 Description of Study Area

7.1.1 Facility

A single facility discharges a moderate quantity of OCS-generated produced waters near Emeline Pass, a major distributary of the Mississippi River delta. Emeline Pass is part of the Baptiste Collette subdelta of the Mississippi River which is located on the east bank of the river just above Venice, Louisiana.

Water depths averaged 3 to 5 m. The water was fresh and currents were swift and related directly to river flow. The river bed was composed of fine, well-sorted, compacted sands. The combination of the swift currents and the hard bed made sampling of bottom water and sediments difficult. The shorelines adjacent to the sampling stations located in Emeline Pass were vegetated with typical freshwater marsh plants. Sample periods were timed for high flow (April 1989) and low flow (October 1989) of the Mississippi River.

Chevron U.S.A. Inc.'s Grand Bay Receiving Station in Emeline Pass was installed in the late 1930s and has been in continual operation since. The average daily discharge for the facility was $3,693 \text{ bbl}\cdot\text{d}^{-1}$ based on a 25-month average from February 1988 - February 1990 (Table 7.1). The volume reported in Boesch and Rabalais (1989a) based on the permit application was $7,300 \text{ bbl}\cdot\text{d}^{-1}$ and was $6,500 \text{ bbl}\cdot\text{d}^{-1}$ on March 1991 (based on operator data, see Table 7.1). The hydrocarbon level of the discharge, reported as oil and grease content, averaged $15 \text{ mg}\cdot\text{l}^{-1}$ for the period February 1988 - February 1990. The chloride level measured for the discharge was 33,040 ppm (59.4 ppt salinity) in February 1990. A combination of heat treatment and gravity separation are used in the facility along with chemicals, including a clarifier, a demulsifier and a bacteriocide. The final holding facility is a large barge. The Grand Bay field has been sold to Greenhill Petroleum Corporation, but Chevron U.S.A. Inc. is still operating the Grand Bay Receiving Station, currently handling production from Main Pass Block 140 (OCS-generated).

As noted above, final separation is in a large barge. The discharge pipe was located adjacent to the barge. Produced water samples were collected from this holding system prior to its entering the discharge pipe. Discharge of the produced water effluent was not directly into Emeline Pass but into a marsh area next to the facility (Figure 7.1). On high river flow, which was the situation in April 1989, the discharge may interchange with the waters of Emeline Pass. During low flow periods, as in the collections of October 1989 and as seen in the aerial photographs taken in November 1988, the discharge flows into the marsh away from the treatment facility.

7.1.2 Study Design

Eleven stations were situated in Emeline Pass in both an upstream and downstream direction of the treatment facility (Figure 7.1). More stations were located downstream in an expected dilution gradient. Similar distances were occupied in both directions. Of the 11 stations, six were designated as "secondary" for vertical sediment core samples; however, adequate vertical samples were difficult to obtain. These also served as stations for which near-bottom waters were collected, often with equal difficulty. The current meter station in April 1989 was a small boat anchor station located close to EP400E. Severe weather in October 1989 precluded the use of a small boat, and current meter readings were made from the R/V *Acadiana*.

No sample stations were located in the marsh behind the discharge treatment facility where the discharge was obviously flowing during low river flow and likely to flow even during high river discharge. The original study design called for the use of the R/V *Acadiana* to operate mid-channel for collection of samples from Emeline Pass. Once the site had been visited on the April flood stage, the actual location of the discharge pipe was discovered.

Data for Emeline Pass are plotted as a function of distance (in meters) and direction away from the point (Station EP0) adjacent to the shoreline where the produced water discharge pipe was located (e.g., EP300W, EP550E).

7.2 Hydrography

7.2.1 Hydrographic Profiles

The water column in Emeline Pass on both collection dates was fresh from surface to bottom at all stations (Tables A.9 - A.10). Conductivity values were slightly higher in October 1989 than in April 1989, but not enough to influence the salinity readout on the CTD. Water temperatures were 15°C in April and 21°C in October.

The water column was well-oxygenated from surface to bottom at all stations during both April and October (Tables A.9 - A.10). Hydrogen sulfide was trace in all near-bottom waters sampled in October.

7.2.2 Dispersion of Effluent

The salinity of the produced water discharge from the Emeline Pass facility averaged 72 ppt (Tables A.9 - A.10). There were no elevated salinities in bottom waters that would identify a produced water effluent. With the volume of water flowing through Emeline Pass, it would not be surprising that the produced water, if it were to enter the pass, would be diluted or swept downstream immediately. The interstitial salinities of surficial sediments were not useful in identifying a salinity signal from an effluent density plume. Only two values were above 1 ppt, but these were within the error of measurement in the chloridometer.

7.2.3 Tidal Current Regime

At Emeline Pass, during both sample periods, no tidal currents were measured. Flow consisted entirely of river flow from west to east, and there was no change in flow direction during the 24 hr of monitoring in April 1989. An anchor station was maintained close to EP400E in 3.5-4 m of water. Current velocities were high with mean velocities varying between 0.7 and 0.9 m·s⁻¹ (Figure 7.2). For example, at 1330 hours on 12 April, the velocity within 25 cm of the bed was 0.6 m·s⁻¹ and the surface velocity was 0.97 m·s⁻¹. These high velocities reflect the high stage and discharge of the Mississippi River in April 1989. During sampling in October 1989, the flow again consisted entirely of river flow with no variation in direction during the 18-hr sample period. Mean velocities were lower than in April, varying between 0.2 and 0.4 m·s⁻¹ (Figure 7.2). This was caused by lower river stages in October. Due to severe weather conditions, the data for October were collected using the current meter from the R/V *Acadiana* rather than a small boat anchor station. Consequently, some of the upper water column readings between 0730 and 1500 on 18 October were affected by the hull of the boat. These readings have been removed from the calculation of mean velocity, and this resulted in slightly lower values for mean velocity during that period.

7.2.4 Velocity Profiles

Velocity profile data from Emeline Pass have been used to calculate shear velocities for both April and October sample periods. Figure 7.2 shows generally consistent values of shear velocities (U_*) in April with occasional peaks to $0.3 \text{ m}\cdot\text{s}^{-1}$. Even apart from the extreme peaks, which may be caused by perturbations in bed roughness, the values were high and indicated significant potential for sediment entrainment at the bed. Observations of box core samples from the bed showed some mud clasts within the sandy sediments. These also indicated a high energy boundary capable of rolling mud balls several centimeters in diameter. Shear velocities in October 1989 (Figure 7.2) were generally lower than in April but were typically greater than $0.2 \text{ m}\cdot\text{s}^{-1}$ with some higher peaks. Again this indicated considerable potential for sediment entrainment and transport at the bed.

7.3 Water Column Contaminants

7.3.1 Hydrocarbons

Tables D.9 and D.10 list the data for volatile and semivolatile hydrocarbons detected in Emeline Pass near-bottom waters for two sample periods. There were no detectable volatile hydrocarbons or PAH; only low levels of saturated hydrocarbons were found in these near-bottom waters. This was a result of the swift currents in the pass and because the produced water was discharged into the marsh and not directly into the pass.

7.3.2 Radionuclides

Pb-210: During April 1989, Pb-210 activities in near-bottom waters were highest at station EP0 (closest to the discharge point) with an activity of $0.79 \text{ dpm}\cdot\text{l}^{-1}$, about 8 times greater than natural levels (Figure 7.3, Table F.3). Pb-210 activities in near-bottom waters elsewhere in the study area were lower (0.02 to $0.67 \text{ dpm}\cdot\text{l}^{-1}$), levels at or 6 times greater than natural water Pb-210 activities.

During October 1989, Pb-210 activities ranged from 0.26 to $0.90 \text{ dpm}\cdot\text{l}^{-1}$, from 2 to 9 times greater than natural levels (Figure 7.3, Table F.3). No general spatial trend was apparent. These Pb-210 activities were greater than observed in April 1989, perhaps reflecting the higher Pb-210 activities of produced waters during this time and/or reduced river flow.

Radium: In all water samples, U-238 and Th-234 activities were below detection levels (<0.5 and $<0.8 \text{ dpm}\cdot\text{l}^{-1}$, respectively). This lack of enhanced uranium and thorium activity indicates strongly that the high radioactivity levels associated with produced waters originate with the radium isotopes and is not supported by radioactive parents of radium which are higher in the decay chain. Total radium is the sum of Ra-226 and Ra-228 activities. The ratio of Ra-226/total Ra varies from site to site for produced waters, but in most cases the Ra-226 activity constitutes more than two-thirds of the total radium activity.

During April 1989, total radium activities in near-bottom waters were highest at station EP100E with an activity of $2.3 \text{ dpm}\cdot\text{l}^{-1}$, approximately natural levels (Table F.3). Total radium activities elsewhere were lower (1.3 to $1.7 \text{ dpm}\cdot\text{l}^{-1}$).

During October 1989, total radium activities ranged from 0.7 to $1.3 \text{ dpm}\cdot\text{l}^{-1}$, within the range of natural levels (Table F.3).

7.4 Sedimentary Characteristics

7.4.1 Grain Size Distributions

In April 1989 the grain size distribution of surface sediment samples were characterized as sandy. All samples were >99% sand (Figure 7.4, Table B.1). Since Emeline Pass is a distributary of the Mississippi River, these bed sediments reflect both the scouring ability of the river flow (Section 7.2.4) and the nature of the river's bed load. Samples from October 1989 were also dominated by sand with less than 5% combined silt and clay, except EP450W which had >25% silt and clay (Figure 7.4). These samples were taken at a lower river stage, and some deposition of finer sediments from the water column during lower flow would account for the change between sample periods. Station EP450W was at the confluence of two minor distributary channels with Emeline Pass. These smaller channels drain the marshes behind the natural levee and the increase in fine sediment content at this station may be a consequence of fine sediment input to the channel from these adjacent wetlands.

7.4.2 Total Organic Carbon (TOC)

The Emeline Pass sites showed the lowest values of TOC found in any of the study areas. Values were always less than 0.5% (Figure 7.5, Table B.1) and the highest value (0.5%) was found at EP1300E during October. These low values are likely caused by the extremely low fine sediment content found in Emeline Pass as organic materials are usually associated with silts and clays. The second highest value of TOC (0.3%) coincided with the highest silt content of any sample at EP450W, but other variations in the low levels of TOC did not follow the changing silt content of the surface sediments.

7.5 Sediment Contaminants

7.5.1 Hydrocarbons

7.5.1.1 Surficial Sediments

In April 1989 (Figure 7.6, Table D.25), the aromatic hydrocarbon concentrations in surface sediments at all stations were very low. No significant quantities of alkylated PAH were detected in any of the sediment samples. Very low levels of some parent PAH were detected at three stations centered around EP400E which had a maximum of 120 ppb of parent PAH. The FFPI values at all of the stations were <0.05 indicating that all of the aromatic hydrocarbons in this region were of pyrogenic origin. The sediments in this region were very coarse relative to most other sites for this study. The low TOC content of these sands was considered to be one factor which contributed to the lack of accumulation of produced water associated alkylated PAH. Aliphatic hydrocarbons were detected in sediments at four stations with the maximum (~2,200 ppb) occurring at EP250E. Total HC concentrations declined rapidly in both directions from this point.

In October 1989, a much more variable but nevertheless consistently low level of parent PAH were detected at several of the stations (Figure 7.7, Table D.26). As before, alkylated PAH were very low, but on this date they were detectable at maximal levels (~40 ppb) at the EP300W site, with lesser amounts detectable at EP550E and EP1300E. The FFPI values at these stations were slightly elevated (~0.3) but still yielded primarily a pyrogenic signature. Aliphatic hydrocarbon concentrations were highly variable in these sediment samples with the minimum occurring at the EPO site nearest to the discharge and higher values observed in both directions along the transect. Several maxima were observed in this distribution, with no clear relationship to the discharge point.

The Emeline Pass site is characterized by high flushing rates and sandy sediments with little sorption capacity for hydrocarbons. The point of discharge for the separation facility is not directly into Emeline Pass. Any produced water hydrocarbons which reach Emeline Pass are likely to be rapidly diluted and transported away from the site. The pattern of aliphatic and alkylated PAH concentrations detected in October suggests that pulses of discharge-related materials may move laterally through the system but may have a very short residence time.

7.5.1.2 Vertical Profiles

For April 1989 only the sediment core from station EP0 was analyzed vertically (Table D.56). As with the spatial distributions of surficial values, very few of the targeted analytes were detected in these sections. All PAH were at trace levels or not detected, and total HC was low at the surface and not detected in the two lower sections.

In October 1989, vertical cores from stations EP0, EP100E and EP450W were analyzed. Data are presented in Table D.57. This table includes a mean of the two sections obtained from each core for comparison with surface station cores. Vertical cores were sectioned at 0-2 cm and from 2 cm to the bottom of the core, either 6, 7 or 8 cm, as compared to 0-5 cm for surface cores. The average of the two vertical sections might be useful for comparison to surface (0-5 cm) core samples, especially if the two vertical sections differed from each other in total length. For the means in Table D.57, in contrast to normal procedure for duplicate analyses, values occurring in one sample but not the other were carried through as the mean. Even with this criteria, only the EP0 mean values resulted in an increase over the surface section and did not substantially change the pattern of the spatial distribution.

C1 and C2 naphthalenes in section 2-7 cm of core EP0 were the only quantifiable alkylated PAH of the three cores analyzed. Trace levels were detected in all cores. Total HC were also low in all three cores with the highest value, 2,500 ppb, recorded in the EP450W core. FFPI was low in this core; the highest value was recorded in core EP0, 0.75 in the 2-7 cm section. EP0 showed quantifiable levels of PAH and total HC only in the 2-7 cm section. The other cores, EP100E and EP450W, showed similar values between the two vertical sections, indicating an even distribution of hydrocarbons among the depths studied. These data show that petrogenic contamination was present near the surface of the sediment at EP0, but saturated HC at points away from EP0 were near background levels and cannot be confirmed as having a produced water origin.

7.5.2 Trace Metals

Trace metal data for Emeline Pass surface sediments are presented in Figure 7.8 and Tables E.9 - E.10. Generally, the sediments sampled in April 1989 showed no clear trends in the metals analyzed. The concentrations of metals varied along the transect with no relationship to the discharge point. The sediments from the October 1989 displayed a maxima for Al, Cr, Cu and Ba at EP700E that was at least five times higher in concentration than at EP0. The increase in metals at EP700E and EP550E were not related to differences in sediment grain size and TOC values which were similar to other stations in the study area. No correlation between trace metal and hydrocarbon distribution was noted at Emeline Pass. No vertical sediment cores were analyzed for trace metals.

7.5.3 Radionuclides

7.5.3.1 Surficial Sediments

Surficial sediment Pb-210 concentrations in Emeline Pass exhibited similar spatial patterns for each of the two sample periods (Table F.11). Surface Pb-210 activities ranged from

0.13 to 0.98 dpm·g⁻¹ during April 1989 and from 0.81 to 2.69 dpm·g⁻¹ during October 1989. Surface sediment Pb-210 activities were correlated somewhat with the percent clay content of the surficial sediments but not with total organic carbon. The lack of correlation was not surprising due to the uniformly sandy, low organic content sediments. Surface sediment Pb-210 activities in coastal environments are typically about 2.0 dpm·g⁻¹ (range: 0.1 to 5.0 dpm·g⁻¹), depending on many factors controlling the sorption reactions (e.g., grain size, percent organic carbon, turbidity in overlying waters). The surface sediment Pb-210 activities observed at Emeline Pass were at or above the upper limit for activities found in natural environments.

7.5.3.2 Vertical Profiles

Sediment Pb-210 activities within the upper 10 cm (length of the cores collected) generally increased in a down-core direction (Figure 7.9, Table F.11). This is different from natural environments where Pb-210 sediment activities decrease down core due to decay and reach a constant background level (~ 0.1 to 0.5 dpm·g⁻¹). Decreasing Pb-210 activities with depth in the core is a prerequisite for calculating sedimentation rates; since these conditions were not present, sedimentation rates could not be calculated for Emeline Pass (see Section 3.6). The pattern observed in Emeline Pass indicated that Pb-210 supply to the sediments had greatly exceeded decay. Because the Pb-210 activities did not decrease to a background level, the inventory calculated from this core gave a minimum estimate of the Pb-210 flux to the area. During April 1989, the minimum Pb-210 sediment inventory at EP0 was 40.5 dpm·cm⁻², more than 1.3 times greater than natural supply.

7.6 Benthic Biota

The benthic macroinfaunal community of Emeline Pass was characterized by few individuals of the following groups: haustoriid amphipods, nemertean worms, and a few species of bivalves, gastropods and polychaetes. Haustoriid amphipods are typical infauna of high energy, sandy marine intertidal beach zones. The high energy, sandy environment at Emeline Pass is the result of fast river currents. Unlike intertidal beach environments, the total organic content of the sediments and food availability of overlying waters was minimal in Emeline Pass. There were few or no individuals of benthic organisms at most Emeline Pass stations (Figure 7.10).

For most benthic community parameters (Tables G.13 - G.15), there were no statistical differences between stations. The exception was number of individuals for October 1989 (Table 7.2); however, these differences were not related to distance from the discharge point. There was a statistically significant interaction of sample date and station location for number of species and number of individuals (Table G.16), but these differences were due entirely to the sample date. There were consistently more species and individuals in benthic collections during low river flow and lower current speeds in October than in April. Still the number of species and number of individuals were low in October.

There were no relationships between the number of species and individuals in the benthic samples to various constituents of the sediments, either grain size distribution, organic content or hydrocarbon contamination. Lack of correlation is not surprising considering the uniform sandy nature of the sediments and overall low organic content including hydrocarbon contaminants. There was also little variability in the benthic community composition with overall low diversity and abundances throughout the transect. There was a slight depression in the number of species and individuals with elevated concentrations of Al and Ni in the surface sediments. The distribution of these elevated metals, however, was not related to distance from the discharge facility.

7.7 Summary

Water flow in Emeline Pass is swift and related directly to river flow. The river bed is composed of fine, well-sorted, compacted sands. There were no elevated salinities in the bottom waters of this freshwater environment that could be attributed to a produced water effluent. There were no detectable volatile hydrocarbons or PAH in near-bottom waters, only low levels of saturated hydrocarbons. Pb-210 concentrations in near-bottom waters were generally within the range of natural values but on occasion reached 6 to 8 times natural water activities.

Consistently non-detectable or low levels of the various hydrocarbon constituents were found throughout the transect. Where calculable, the FFPI values indicated primarily a pyrogenic signature. Pb-210 inventories indicated a flux to the area, but this was only 1.3 times greater than natural supply. Elevated levels of some trace metals were detected, but these higher values were not related to distance from the discharge facility.

Basically, the high flushing rates and dilution potential of the Pass along with a river bed of sandy, low organic content sediments provided an environment with little capacity for accumulation of hydrocarbons. In addition, the point of discharge from the treatment facility was not directly into Emeline Pass, and it is unlikely that much of the discharge effluent enters the pass from near the facility.

The benthic fauna of Emeline Pass was characterized by few species and low abundances. Numbers of species and individuals increased in the fall (low river flow period) compared to the spring (high river flow period). The depauperate fauna was a characteristic of the fine-grained, sandy, low organic sediments and the high energy river flow.

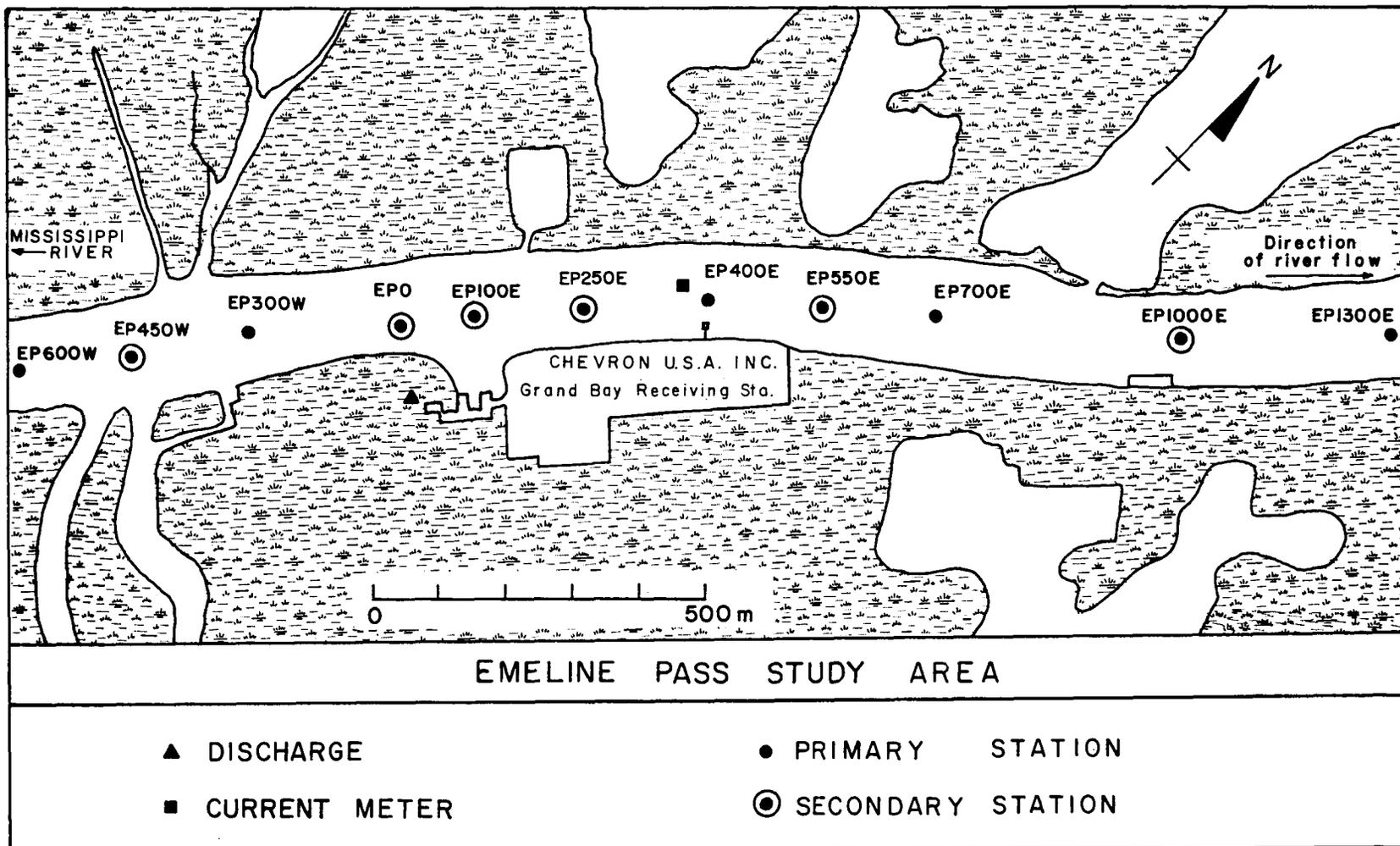


Figure 7.1. Location of stations at Emeline Pass study area.

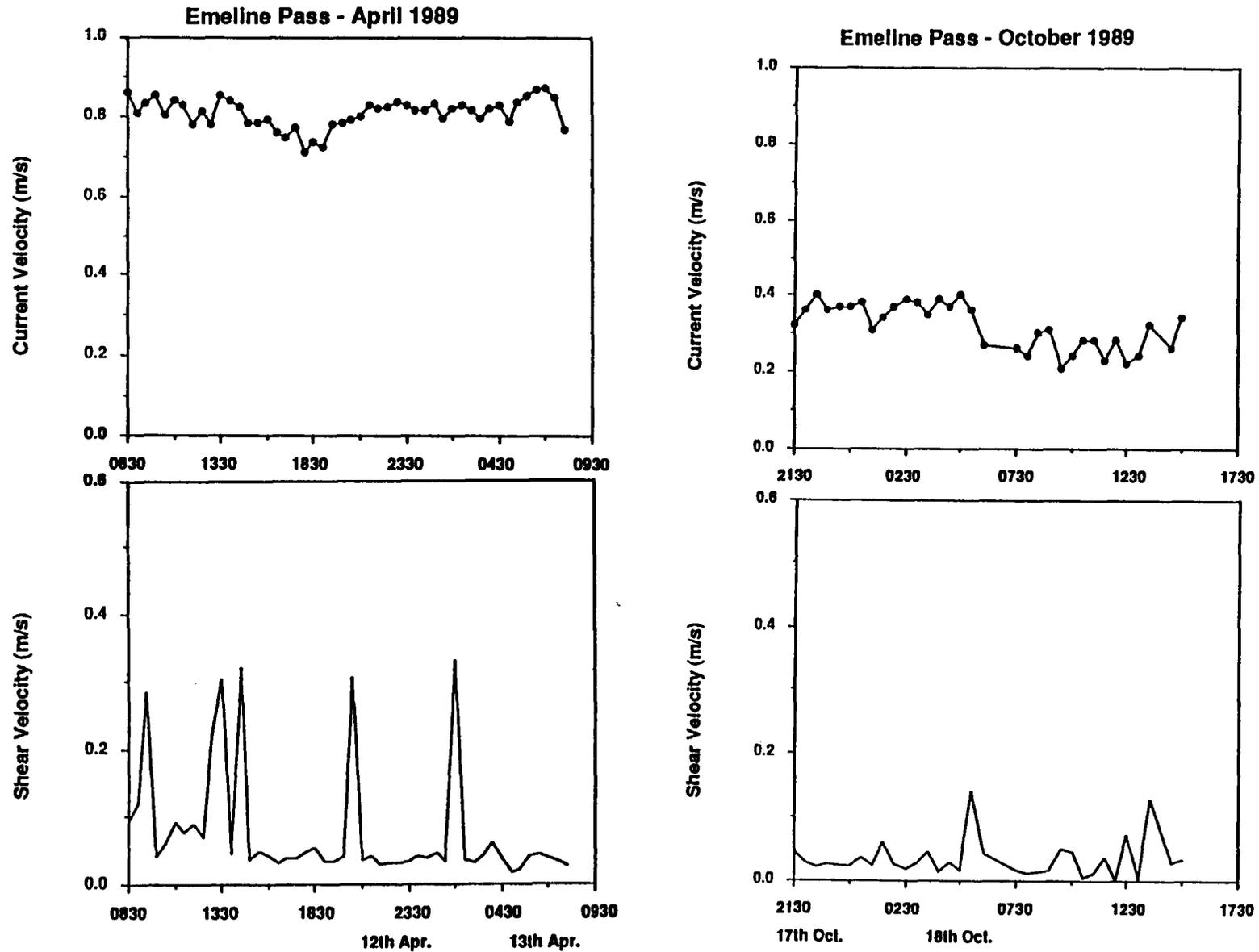
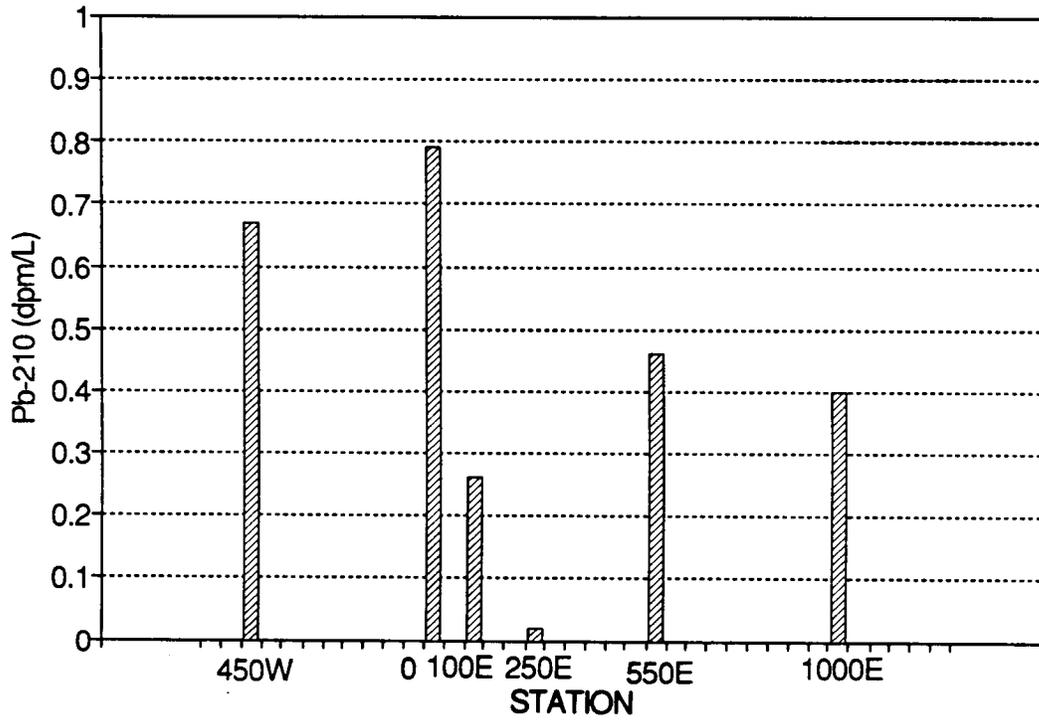


Figure 7.2. Mean current velocity variation and calculated shear velocities for Emeline Pass, April and October 1989.

EMELINE PASS: APRIL 1989



EMELINE PASS: OCTOBER 1989

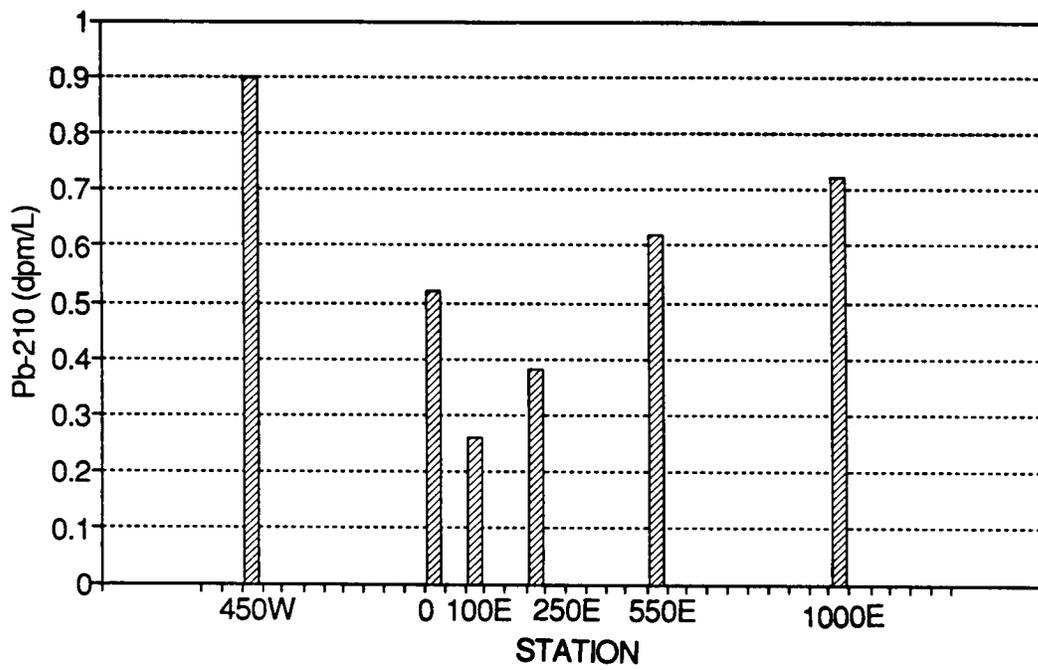


Figure 7.3. Spatial distribution of Pb-210 activities in Emeline Pass near-bottom waters, April and October 1989.

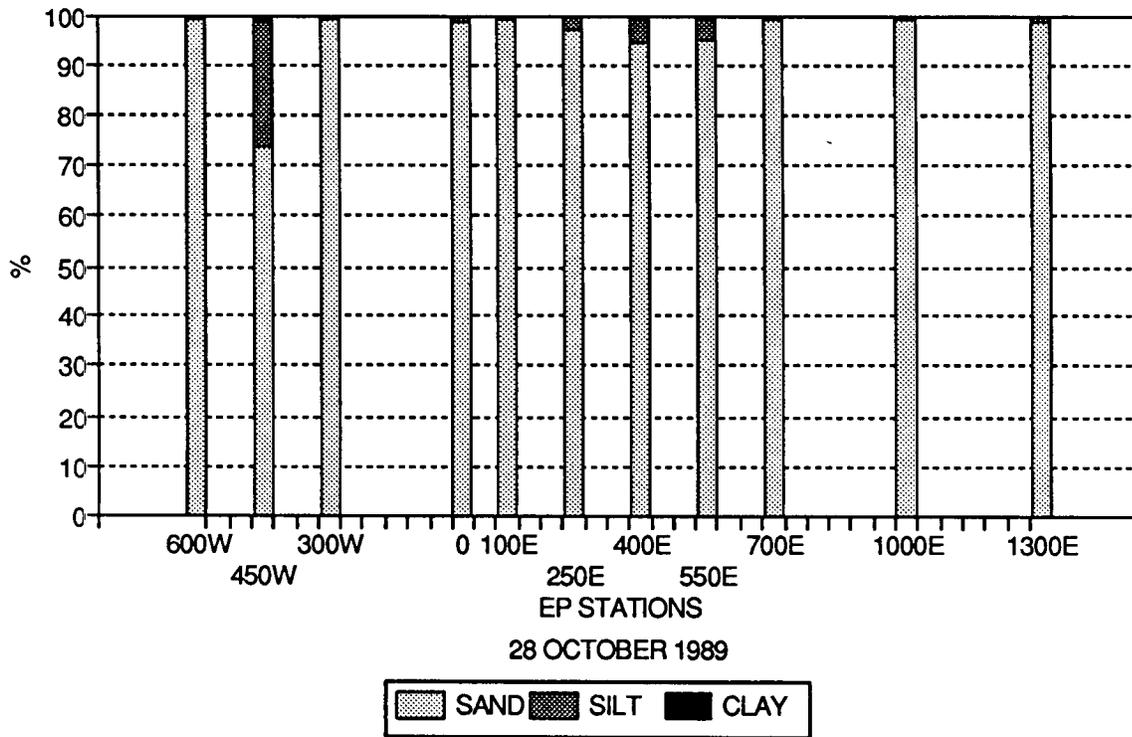
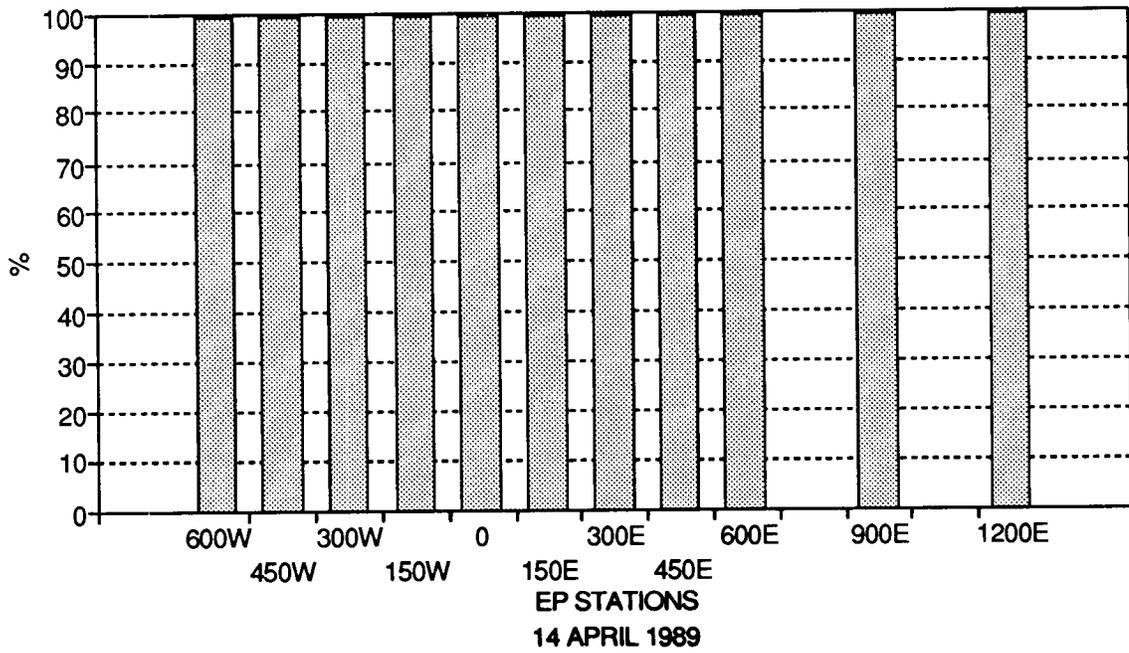


Figure 7.4. Spatial distribution of surface sediment grain size from Emeline Pass, April and October 1989.

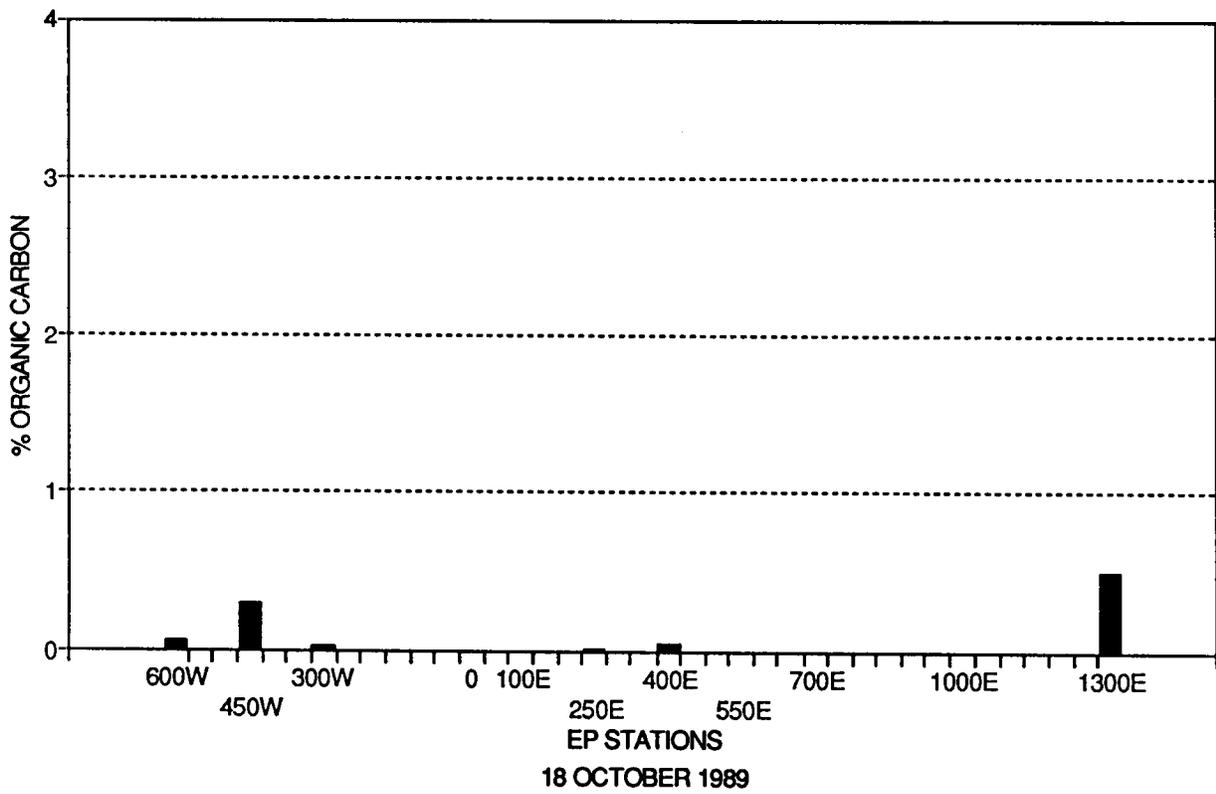
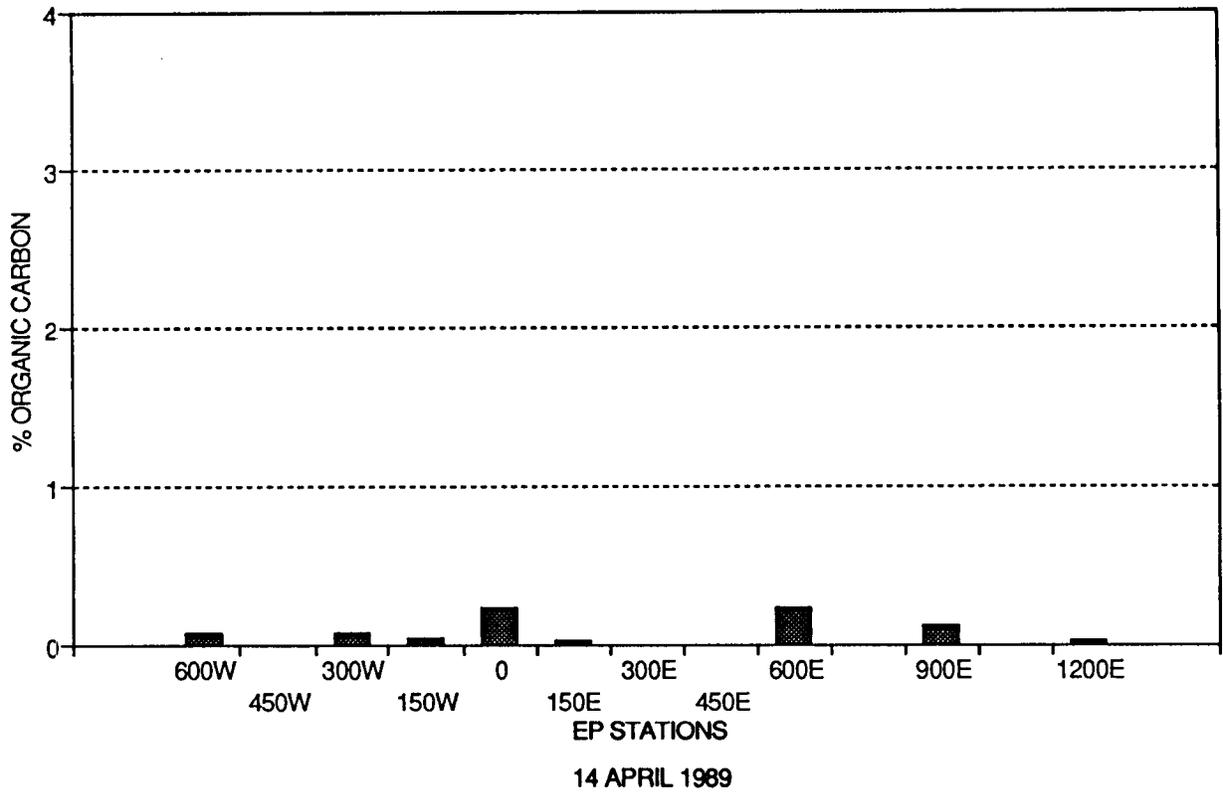


Figure 7.5. Spatial distribution of percent total organic carbon in surface sediments from Emeline Pass, April and October 1989.

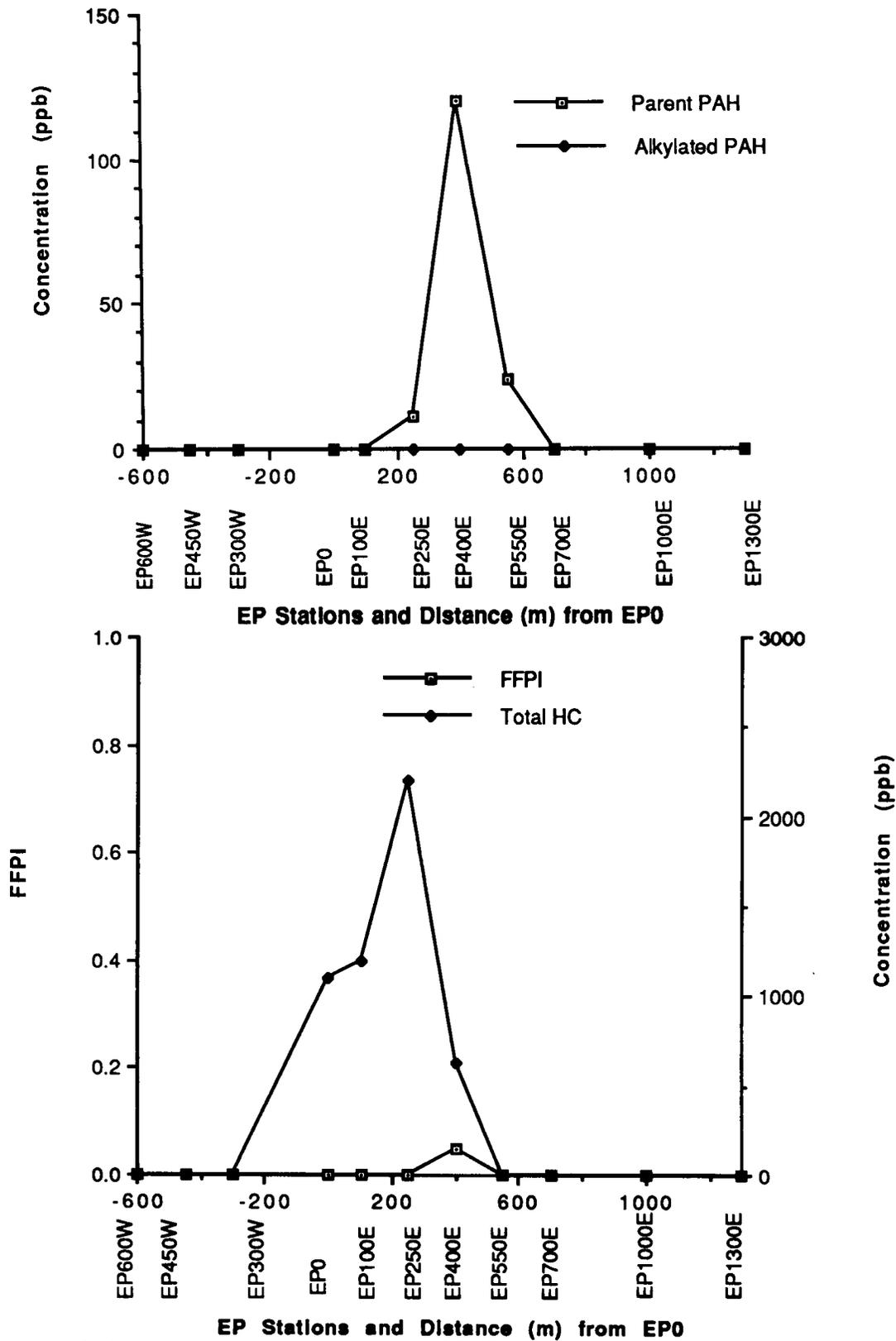


Figure 7.6. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from Emeline Pass, April 1989.

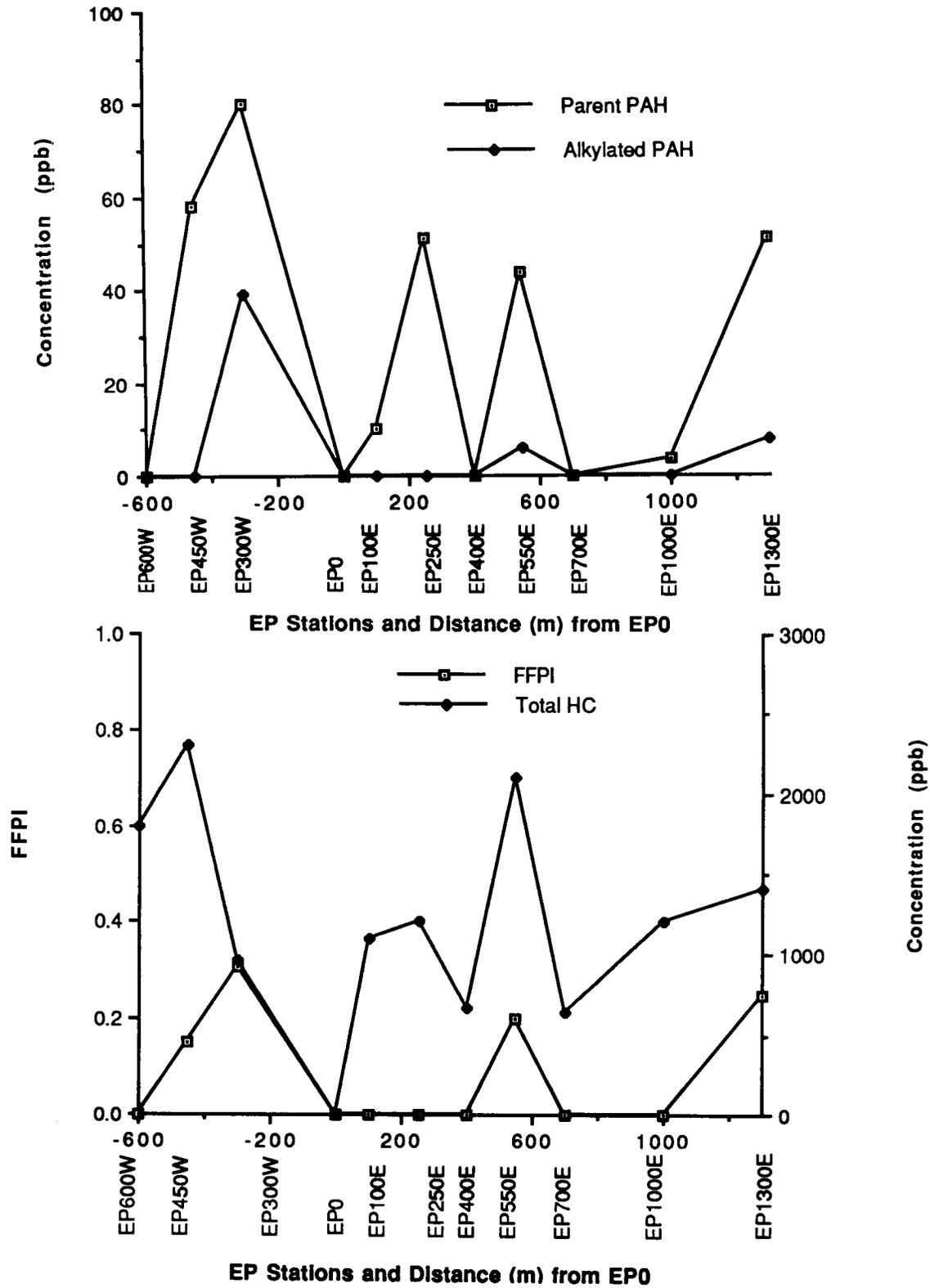


Figure 7.7. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from Emeline Pass, October 1989.

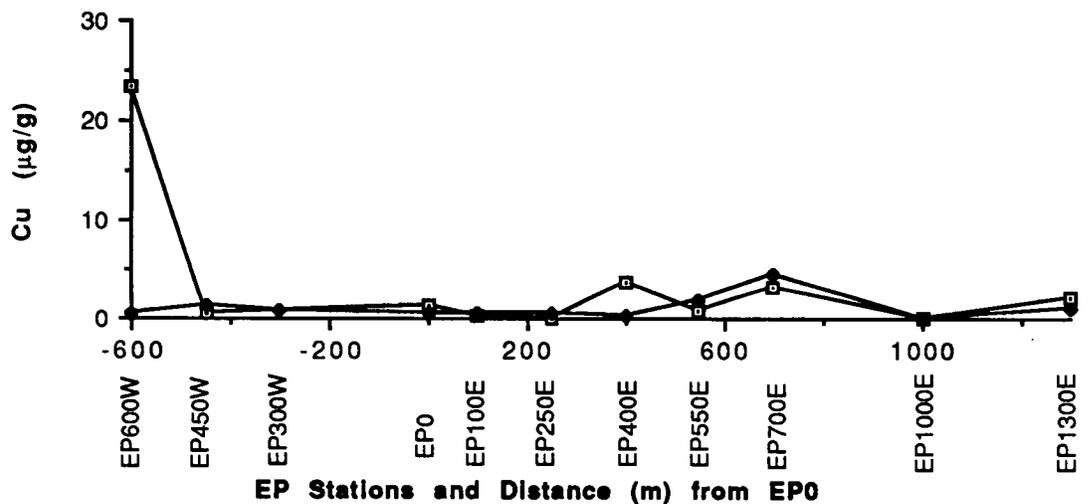
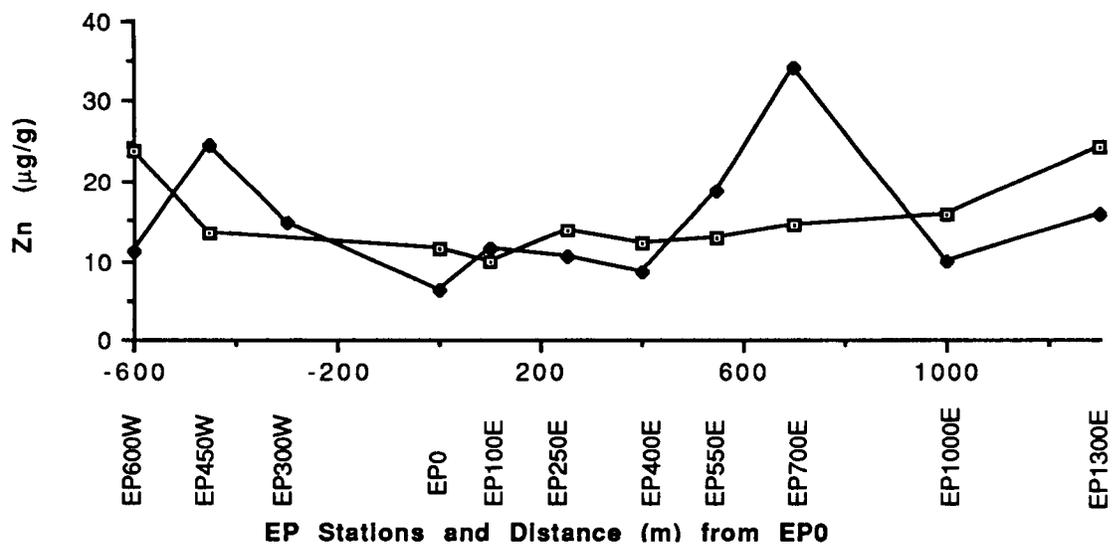
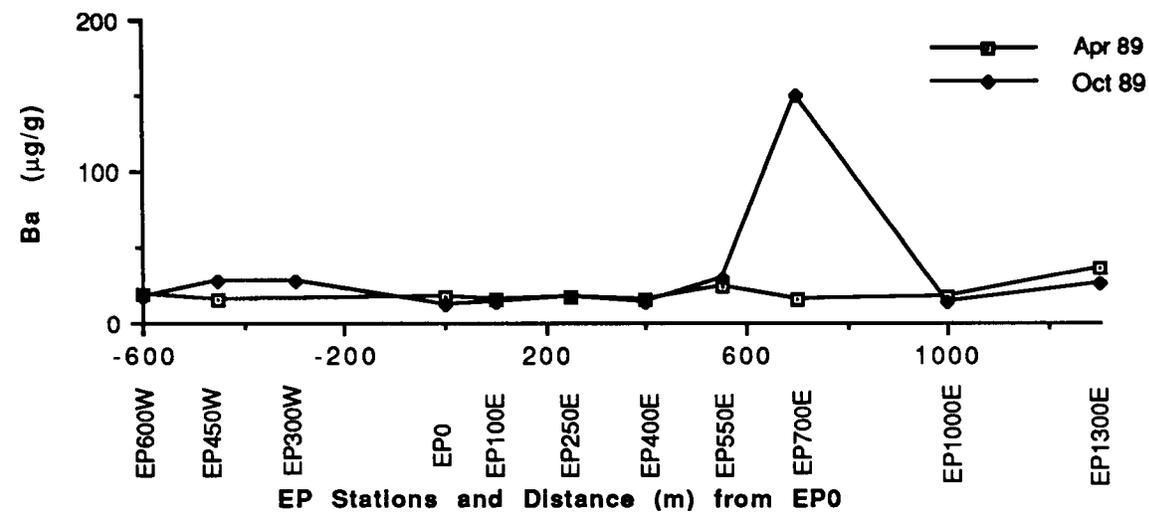


Figure 7.8. Spatial distribution of selected trace metal concentrations in surface sediments from Emeline Pass for two sample periods.

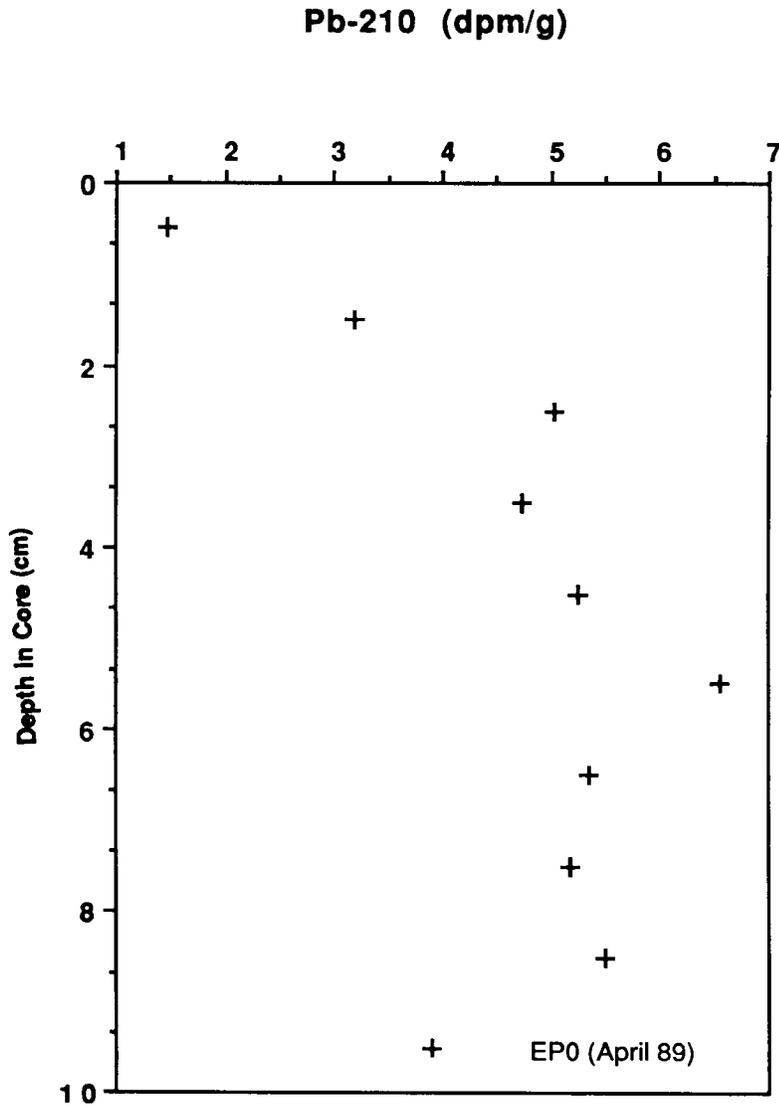


Figure 7.9. Pb-210 activities in vertical sediment core sections from station EPO in Emeline Pass, April 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

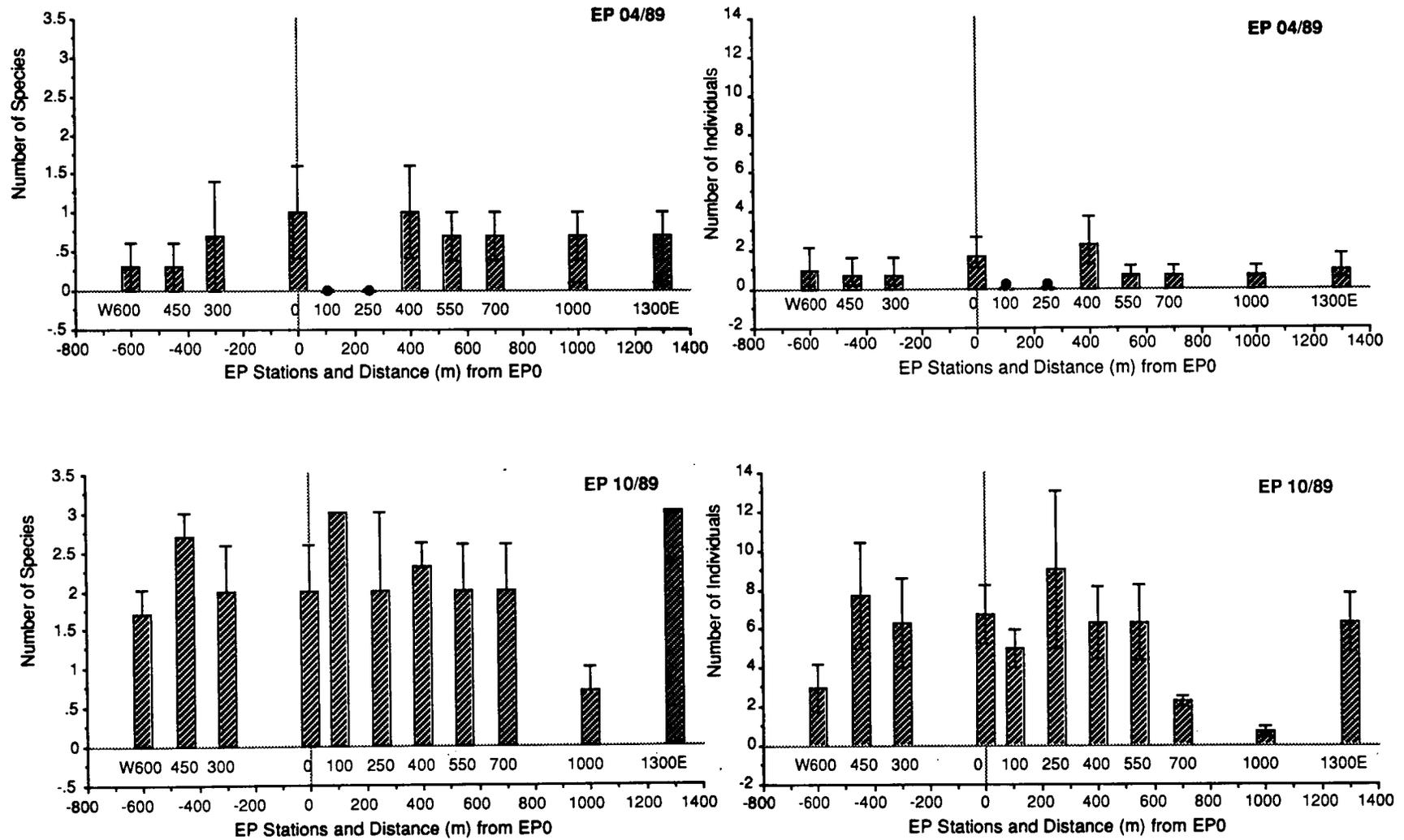


Figure 7.10. Spatial distribution of number of species per replicate (mean \pm standard error) and number of individuals per replicate (mean \pm standard error) for Emeline Pass, April and October 1989.

Table 7.1 Average daily discharge (bbl·d⁻¹) and oil and grease content (mg·l⁻¹) of produced waters from the Grand Bay Receiving Station in Emeline Pass. (Data provided by operator.)

Date	Facility
	Grand Bay Receiving Station
04/89	
Discharge	2,927
Oil and Grease	10
11/89	
Discharge	1,688
Oil and Grease	9
Average Discharge	3,693*
Average Oil and Grease	15*
Discharge as of 03/91	6,500

*Mean of 25 monthly sample dates from 02/88 - 02/90.

Table 7.2. Duncan's multiple range test for Emeline Pass study area, October 1989; underlined stations are not significantly different from each other.

Number of Individuals (natural log transformed):

450	0	250	1300	550	400	300	100	600	700	1000
W		E	E	E	E	W	E	W	E	E

Chapter 8

EUGENE ISLAND STUDY AREA

8.1 Description of Study Area

8.1.1 Facility

The Shell Offshore, Inc. Eugene Island facility is located on the shallow inner continental shelf offshore of Atchafalaya Bay just outside of the remnant oyster reefs which demark the lower end of Atchafalaya Bay. The site is influenced by alternate deposition of sediments from the Atchafalaya River and wave scour of deposited sediments. Tidal currents are a significant factor in the resuspension and transport of sediments in this area. The region also receives significant freshwater discharge from the Atchafalaya River. Because of the shallow water depth (2 m) and the broad expanse of the shallow inner continental shelf, it is unlikely that this area is affected by seasonal bottom water hypoxia.

The ambient salinity of the Eugene Island Block 18 area is strongly related to that of the discharge of the Atchafalaya River as it mixes with the nearby Gulf of Mexico. Salinities at the stations sampled during the two study periods ranged from 0 to 27 ppt. In May 1989 the water column was well-mixed across most of the study area, but salinities from surface-to-bottom ranged from 4 to 25 ppt across a 2-km wide distance. In November 1989, a strong salinity wedge was recorded at most stations with surface to bottom differences as great as 19 ppt.

The produced water discharge for the Eugene Island study site is Shell Offshore, Inc.'s Eugene Island Block 18M platform. The current system, a multi-cell unit, was installed in 1987. The original system was a CPI (corrugated plate interceptor) cell. The field has been discharging for 30 years. The average discharge rate for the facility is 21,000 bbl·d⁻¹ based on a 25-month average for January 1988 - January 1990 (Table 8.1). The total volume reported in Boesch and Rabalais (1989a) based on the permit application was 30,000 bbl·d⁻¹. Of the current total discharge, 100 bbl·d⁻¹ are generated on the Federally-controlled OCS; the remainder is from the State's territorial sea. The hydrocarbon levels of the discharge, reported as oil and grease content, averaged 18 mg·l⁻¹. The average chloride for the discharge was 100,000 ppm (180 ppt salinity). Chemical additives are used in the treatments at this facility. A change in chemicals took place between March and June 1989.

8.1.2 Study Design

Two transects of five stations each extended from the platform, centered on Station E10 on the southeast corner of the platform where the discharge of produced waters entered the open Gulf of Mexico (Figure 8.1). Transect A was established in an expected down-plume, down-gradient direction (if one existed) at 225° from north. Nearshore currents generally flow from east to west in this area, and sediments and freshwater entrained in the coastal boundary layer also move from the east to west. The heading of 225° was also dictated by the large number of pipelines which feed into platform M. The R/V *Acadiana* lost one anchor during the operation (pipeline snag). Stations along transect A were at 50, 100, 250, 500 and 1000 m from the discharge. Because of the complexities of pipelines in the area, transect B was located due north. The size of platform M precluded a 50- and 100-m distant station from the discharge along the north heading. The first station was located at 200 m from the discharge, the second at 300 m from the discharge; then at 500, 700 and 1000 m. Stations E10, E1A50, E1A100, E1A250 and E1A500 were designated "secondary" stations where vertical sediment cores and near-bottom water samples were taken. Current meter readings were taken from the R/V *Acadiana* rather than from a small boat at anchor. At night when stations were not being sampled, the

Acadiana was positioned near EIA250. During collections of water column and benthic samples, the current meter data were taken wherever the *Acadiana* was on location.

Sample periods were timed for high flow (May 1989) and low flow (November 1989) of the Atchafalaya River. Adverse weather conditions and rough seas during the May 1989 trip prevented completion of samples at stations EIB700 and EIB1000. All stations were successfully sampled during November 1989. The data for the Eugene Island study area are plotted as a function of distance away from the point of the produced water discharge.

8.2 Hydrography

8.2.1 Hydrographic Profiles

Hydrographic conditions at the Eugene Island Block 18 study area were considerably different on the two sample dates and reflected the strong influence of the Atchafalaya River discharge on the shallow inner continental shelf (Figures 8.2 - 8.3, Tables A.11 - A.12). In May 1989 the winds were strong and sea conditions were rough with waves of 1.5 to 2 m affecting collection of data later in the day. In November 1989 the sea state was calm. On both occasions the freshwater discharge of the Atchafalaya River was apparent in the water column profiles.

In May 1989 the salinity profiles for the stations sampled (Figure 8.2) varied from well-mixed with surface-to-bottom salinities of 16, 20 or 24 ppt to moderately and highly stratified. At station EIA500 the surface salinity was 15 ppt and the bottom salinity, 19.4 ppt. At station EIA250, however, the surface salinity was 5.4 ppt and the bottom salinity, 23.1 ppt. Water temperatures were 24 to 26°C. The water column was well-oxygenated at all stations.

In November 1989 the salinity profiles were similar for all stations with the exception of EIA100 (representative profiles in Figure 8.3). Surface salinities were 0 ppt and bottom water salinities ranged from 11.4 to 18.6 ppt. The steepest gradient in salinity occurred between 1.5 and 2 m depth. Surface salinity for station EIA100 was 0 ppt, but the bottom water salinity was only 3.3 ppt. The depth of the water column at this station was only 1.6 m as compared to an average of 2 m for the other stations around the platform. The water depth for station EIA100 was also recorded at 0.5 m less than the surrounding stations in May 1989, indicating a topographically higher area. Water temperatures in November were 15 to 16°C. The water column was well-oxygenated at all stations. In November 1989 sulfide levels were trace in near-bottom water samples.

8.2.2 Dispersion of Effluent

The average salinity of the produced water discharge from Eugene Island Block 18 platform was 142 ppt. An effluent density plume for the produced water discharge was not evident from the water column CTD casts taken around the platform. Surface-to-bottom salinity differences were a feature of the freshwater discharge of the Atchafalaya River mixing with the inner continental shelf waters. The interstitial salinities of surficial sediments were not unusually elevated above the ambient levels during the period of study, with the exception of station EIA100 (Figure 8.4). In both May and November, this station showed the greatest departure from the salinity of the overlying water. The differences seen at station EIA100 may be related to its topographically higher location.

8.2.3 Tidal Current Regime

Tidal current monitoring at Eugene Island was conducted from the R/V *Acadiana* rather than from a small boat at anchor because of the remote location and sea conditions. At least 8 hours of readings at the beginning of each period were obtained at anchor close to EIA250.

Subsequent readings were taken at the various stations as sampling proceeded. In May 1989, monitoring was stopped at 1800 because of sea conditions. In November 1989, a complete 25-hr data set was collected. During May 1989 there was no significant change in current direction for the entire sampling period. The current was between west and northwest and was accompanied by strong winds and moderate seas which eventually stopped monitoring. Mean velocities varied considerably (Figure 8.5) from $0.2 \text{ m}\cdot\text{s}^{-1}$ to $0.65 \text{ m}\cdot\text{s}^{-1}$. The pattern of variation suggested that there was some influence of the predicted unequal semi-diurnal tide on the magnitude of the current if not the direction. In November 1989 a clear tidal signature was apparent in the data. Flood velocities were to the northeast and ebb was to the southwest. Velocities were low (Figure 8.6), typically less than $0.2 \text{ m}\cdot\text{s}^{-1}$. However, this is an open shelf location where tidal flow is not channelized and high velocities are not expected under normal tidal conditions. The predicted tide for this sampling period was a transitional tide between diurnal and semidiurnal and this may account for the weak ebb tides between 0600 and 1000 on 21 November.

8.2.4 Velocity Profiles

The pattern of shear velocities derived from the velocity profiles for May 1989 (Figure 8.5) closely followed the variations in mean velocity described above. Generally the shear velocities were greater than $0.01 \text{ m}\cdot\text{s}^{-1}$, indicating potential for sediment entrainment at the bed. The major peak in shear velocity between 0800 and 1200 on 17 May would have resulted in high bed shear stresses and sediment resuspension. In November 1989 the shear velocities showed tidal variation (Figure 8.5). Again, values were high, especially during the late flood and early ebb stages, allowing sediment entrainment and transport. There was some asymmetry with higher shear velocity values on the ebb than on the flood. Likely direction of sediment transport for the ebb stage would have been to the southwest.

8.3 Water Column Contaminants

8.3.1 Hydrocarbons

The data for near-bottom waters are presented in Tables D.11 - D.12. There were no volatile hydrocarbons or PAH detected during May 1989. Volatiles and PAH were found in near-bottom water sampled at E10 during November 1989. Small amounts of benzene were detected at stations EIA100 and EIA250 at decreasing levels away from the discharge. A trend indicating the platform as the source could not be totally confirmed, because the volatile sample from EIA50 was lost due to a broken bottle. No detectable levels of PAH were found in any other near-bottom water samples besides E10. The results from this study are similar to other studies involving separator platforms in open water (Armstrong et al. 1979). Typically, there are detectable amounts of hydrocarbons in the immediate vicinity of the discharge, but concentrations rapidly decrease not very far from the source.

8.3.2 Radionuclides

Pb-210: During May 1989, Pb-210 activities in near-bottom waters were highest at the stations closest to the discharge point (E10, EIA50 and EIA100) with activities decreasing from $2.18 \text{ dpm}\cdot\text{l}^{-1}$ to $1.17 \text{ dpm}\cdot\text{l}^{-1}$ at EIA500 (Table F.3). These activities are about 12 to 22 times greater than natural levels.

During November 1989, Pb-210 activities were much lower, ranging from 0.02 to $0.09 \text{ dpm}\cdot\text{l}^{-1}$ (Table F.3), all within the range of natural levels. No general spatial trend was apparent. These Pb-210 activities were lower than observed in May 1989, perhaps reflecting the lower Pb-210 activities of produced waters during this time period.

Radium: In all water samples, U-238 and Th-234 activities were below detection levels (<0.5 and <0.8 dpm·l⁻¹, respectively). This lack of enhanced uranium and thorium activity indicates strongly that the high radioactivity levels associated with produced waters originate with the radium isotopes and is not supported by radioactive parents of radium which are higher in the decay chain. Total radium is the sum of Ra-226 and Ra-228 activities. The ratio of Ra-226/total Ra varies from site to site for produced waters, but in most cases the Ra-226 activity constitutes more than two-thirds of the total radium activity.

During May 1989, total radium activities in near-bottom waters ranged from 3.1 to 16 dpm·l⁻¹ (Table F.3), generally increasing with increased salinity. These activities were about 1.5 to 8 times greater than natural levels.

During November 1989, total radium activities were uniform across the study area (ranging from 5.7 to 6.6 dpm·l⁻¹), with the exception of station EIA100 (1.1 dpm·l⁻¹) which was much lower than surrounding stations (Table F.3). Station EIA100 also had a lower salinity than surrounding stations (3 ppt relative to 11-17 ppt for others). Total radium activities in the area were at the upper range of natural levels.

8.4 Sedimentary Characteristics

8.4.1 Grain Size Distribution

Surface grain size distributions at Eugene Island in both May and November 1989 were dominated by silts. All samples were >80% silt with clay typically 5-10% and sand <5% (Figure 8.6, Table B.1). Clay content was lowest at EIB200 and EIB300 in May and was also low at these stations in November. Sand content was highest at EIO and EIA50 in May and at EIO and EIB700 in November. Overall the sediments can be characterized as clayey silts which represented the sediments supplied from the Atchafalaya River. Greater sand content at EIO, close to the platform, may be accounted for by materials introduced into the area during platform construction and/or maintenance. Sedimentation rates in this area, however, are high and surface sediments should reflect recent depositional conditions.

8.4.2 Total Organic Carbon (TOC)

Despite the high silt content of sediment at the Eugene Island site, TOC values for surface samples were low during both May and November 1989. Only three sites had TOC values greater than 1% [EIA500, EIA1000 and EIB200] (Figure 8.7). The lowest value in May was 0.5% at EIO, the station closest to the discharge point. In November values varied from 0.7% at EIB700 and EIA100 to 0.9% at EIA500 (Figure 8.8). There was no clear pattern to the variations in TOC content. Low values would reflect expected high sedimentation rates in this area; however, sedimentation rates could not be calculated because of the high Pb-210 flux to the sediments. The TOC samples were taken from the surface sediments which are those most recently deposited and which have had little time for colonization by organisms.

8.5 Sediment Contaminants

8.5.1 Hydrocarbons

8.5.1.1 Surficial Sediments

Alkylated PAH associated with the discharge were detected in the sediments closest to the discharge point (Figures 8.8 - 8.9, Tables D.27 - D.28). A maximum value of ~2,000 ppb was detected at EIO with very low but detectable levels at EIA50 and EIB200. Low, but detectable, parent PAH concentrations were observed throughout the region. The values of FFPI

observed in May 1989 were highest at the discharge point and at EIA50 but decreased rapidly to values <0.3 at all of the other stations. The origins of the parent PAH at this site may be the large diesel powered compressors used to feed the natural gas produced at the site into pipeline systems or combusted fuel from the many supply vessels that service the area. Aliphatic hydrocarbons were detectable in all sediment samples with a maximum value observed at EIO and decreasing rapidly along both transects away from the discharge.

In November 1989, the alkylated PAH content of the sediments in the region surrounding the discharge was similar to those in May. Highest levels were observed in the EIO and EIB200 sediments with lesser amounts in the EIA50 sample. FFPI values >0.9 were measured for the two highest stations, but fell to 0.6 at the EIA50 site. All other FFPI values were <0.2, confirming the more dominant parent PAH content of the sediments further from the discharge. Aliphatic hydrocarbon concentrations near the discharge were elevated at EIO and EIB200 and much lower at all other stations. Where they were highest, total HC concentrations were higher than those observed in May 1989.

Hydrocarbon contamination around the Eugene Island produced water discharge is typical of open water facilities. It is interesting to note that, even with the great potential for dilution and dispersion of particulates at a site such as this, produced water-associated hydrocarbons were still detectable out to 200 m. The fact that the zone of impact extended 200 m to the north and only 100 m to the southwest may suggest that current direction and speed will vary significantly with season and weather, favoring deposition in certain directions over others.

8.5.1.2 Vertical Profiles

All vertical sediment cores taken during November were analyzed; however, only cores from EIO and EIA50 were analyzed from May (Figure 8.10). This was done for three reasons: 1) spatial distributions were similar between the two collections, 2) only the two stations nearest the discharge showed contamination with petroleum hydrocarbons, and 3) cores from the May collection may have been disturbed due to weather conditions at the time of the cruise. For Figures 8.11 - 8.12 showing the hydrocarbon depth profiles for November, note that for stations EIA100 through EIA500 the concentration scale is one-tenth of that used for data from stations EIO and EIA50 in November. Data are detailed in Tables D.58 - D.64.

8.5.1.2.1 May 1989

EIO: Aromatic hydrocarbons in this core were dominated by alkylated PAH. No trends with depth were observed with the parent PAH, which averaged ~100 ppb over the entire length of the core. The distribution of alkylated PAH in the core showed a large subsurface maximum between 20 and 25 cm of greater than 5,000 ppb. A surface peak was also observed (2,100 ppb), with alkylated PAH concentrations ranging from 1,200 to 2,100 ppb in the top 5 cm. Alkylated PAH concentrations between 10 and 15 cm in the core dropped to as low as 36 ppb. Below the subsurface maximum a second minimum of 100 ppb was observed at 30 cm. FFPI values calculated for the PAH data from this core indicated that petrogenic PAH were the dominant PAH present. FFPI values were >0.7 in sections except those that had the very low alkylated PAH content. Naphthalenes were the major alkylated PAH present followed by fluorenes. Lesser amounts of phenanthrenes were detected in some core sections. Only trace amounts of dibenzothiophenes were detected.

Total hydrocarbons profiles in this core were very similar to those for the alkylated PAH. The same subsurface and surface maxima were observed. Decreased total HC concentrations were observed between 2 and 15 cm in the core and a second minimum was observed just below the subsurface maximum at 30 cm. R/T ratios for the hydrocarbons in the core were generally less than 0.15 indicating advanced weathering. However, in both the subsurface maximum

region and the surface section, values were 0.30 and 0.24, respectively, suggesting that the hydrocarbons in these sections may not have completed the weathering process.

EIA50: Aromatic hydrocarbon concentrations in this core were much lower than in the E10 core. Parent PAH concentrations were low and averaged 130 ppb over the length of the core. A subsurface maximum value for parent PAH of 320 ppb was observed at 15 cm. Alkylated PAH concentrations were maximal at 10 cm (650 ppb). An increasing gradient of alkylated PAH was observed between the surface section of the core (430 ppb) and this maximum. Below this level, concentrations of alkylated PAH decreased dramatically to trace levels.

Aliphatic hydrocarbon concentrations in this core followed the same trends as the alkylated PAH except that the subsurface maximum for total HC was observed in the 5 cm section. R/T ratios for the hydrocarbons in this core all indicated advanced weathering (<0.11) except for the surface segment (0.36) which contained more recently deposited material.

8.5.1.2.2 November 1989

E10: Parent PAH concentrations in this core were very low relative to the alkylated PAH and were relatively constant throughout the core, averaging 200 ppb. As was seen in May 1989, there was a high subsurface maximum (25,000 ppb), however, the maximum occurred in the 10-15 cm section rather than the 20-30 cm sections as observed in May. Concentrations in the 20-30 cm section were nearly identical to the May core, suggesting that all of the alkylated hydrocarbons seen in the upper sections of the November core were rather recent deposits. Recall that the upper sections of the May core had some of the lowest alkylated PAH concentrations in that core. FFPI values calculated for the November core were uniformly greater than 0.8 and did not appear to vary much with depth. Alkylated naphthalenes were by far the dominant PAH present averaging 86% of the PAH detected. Fluorenes and phenanthrenes made up the balance of the alkylated PAH present. Dibenzothiophenes were only present in trace amounts.

Aliphatic hydrocarbons exhibited the same distribution patterns as alkylated PAH. A subsurface maximum of 460,000 ppb was observed in the 15-20 cm section of the core just below the alkylated PAH maximum. Total HC concentrations in the 20-30 cm sections of the core were similar to those observed in the May core. R/T ratios for this core indicated that much of the HC fraction was less weathered than in the May core. Values as high as 0.5 were observed with most sections exhibiting R/T ratios >0.35 . No values <0.1 , which were typical for the May core, were observed in the November core.

EIA50: Parent PAH concentrations were similar to those observed in May, averaging 96 ppb. No patterns with depth were observed for the parent PAH. Alkylated PAH concentrations were highly variable exhibiting several maxima with intervening minima. The greatest alkylated PAH concentrations were observed in the 15-20 cm and 5-10 cm sections (900 and 420 ppb, respectively). Alkylated PAH were at very low levels or trace levels in all other sections below the surface, which contained 57 ppb of alkylated PAH. The FFPI values showed a strong petrogenic signal only for the surface segment and the 15-20 cm segment. Most other sections had FFPI values between 0.1 and 0.3, indicating a mixture of PAH dominated by pyrogenic PAH.

Total hydrocarbons core showed a subsurface maximum of 48,000 ppb in the 15-20 cm segment and a maximum of 62,000 ppb just below the surface (2-5 cm). The R/T ratios for this core yielded values <0.15 for all sections, except the 15-20 cm section, which had a value of 0.27 indicating that the weathering process was incomplete in this section.

EIA100: The aromatic fraction of all sections was dominated by pyrogenic PAH which averaged 53 ppb over the length of the core but were highly variable. A maximum parent PAH concentration of 120 ppb was observed at the surface. FFPI values calculated for the core were all less than 0.15, indicating no significant inputs of petroleum hydrocarbons at this station over time.

Aliphatic hydrocarbons were detectable in all sections. Maximal values ranging from 17,000 to 27,000 ppb were measured between 2 and 15 cm. Most other sections contained between 4,900 and 11,000 ppb total HC. R/T ratios for all sections were <0.11, indicating advanced weathering had occurred.

EIA250: Parent PAH were the dominant aromatic hydrocarbons. Concentrations ranged from trace to 160 ppb, with an average of 71 ppb. A subsurface maximum was observed at 30-35 cm. Only trace amounts of any alkylated PAH were detected, thus FFPI values were uniformly low.

Total HC concentrations were relatively constant in the upper sections, averaging ~10,000 ppb from 0 to 25 cm. Higher, relatively constant, concentrations of 19,000 ppb were observed in the 25-40 cm section. This corresponded to the increase in parent PAH seen in these sections. R/T ratios for the hydrocarbons were all less than 0.15.

EIA500: As at the EIA250 station, parent PAH were the only aromatic hydrocarbons detected in significant amounts in this core. Parent PAH were detectable at only trace levels in the top of the core but exhibited variable but detectable levels ranging from 37 to 100 ppb. Two subsurface maxima, at 10-15 cm and 25-30 cm, were observed with intervening minima. Detectable alkylated PAH were only found in the 30-37 cm section (33 ppb). All other sections contained only trace levels of alkylated PAH. FFPI values were uniformly low, increasing to 0.33 in the bottom segment due to the presence of detectable alkylated PAH at low levels.

Total HC concentrations were highly variable, ranging from 4,000 to 11,000 ppb with an average of 7,500 ppb. The profile shows several maxima and minima suggesting variable inputs to the region over time and/or mixing. R/T ratios were all below 0.3 with most sections exhibiting a ratio of 0.17 or less.

8.5.2 Trace Metals

8.5.2.1 Surficial Sediments

Data for surface sediments from Eugene Island are detailed in Tables E.11 - E.12 and shown in Figure 8.13. Barium displayed maximum values in both months at station EI0. Barium concentrations decreased along both transects away from the discharge point. This was the same pattern as for hydrocarbons, suggesting similar sources for analytes. No other metals displayed a similar pattern in sediments from May. The concentration of barium measured at EI0 from November 1989 was 10 times higher than in May. Other metals did not display the same pattern as Ba, but were in higher concentration than the May samples with the exception of aluminum. Concentrations of other metals in sediments sampled in November 1989, tended to be higher along the A transect, especially Al, Cr, V, Zn and Cd. The sediments in the immediate vicinity of the discharge definitely showed that they were impacted, but this did not extend beyond 50 m.

8.5.2.2 Vertical Profiles

Vertical sediment cores from stations EI0, EIA50 and EIA100 of the November 1989 collection were analyzed for trace metals (Tables E.24 - E.26). Figure 8.14 shows the Ba, Zn

and Ni depth profiles for each core. Trace metal concentrations in general did not appear similar to the patterns for hydrocarbon data.

E10: Barium concentrations were highest in this core of the three analyzed. The Ba value for the surface section, 2,500 ppm, was the highest concentration noted for all surface and vertical sections analyzed. In sections below the surface, Ba concentrations dropped, but the average, 640 ppm, remained higher than for other cores. Aside from the maxima in the surface section, Ba concentrations showed a general increase towards the middle sections (10-15 cm), followed by a general decline nearer the bottom, somewhat similar to hydrocarbon data, which showed a sharp increase in the middle of the core. Zn concentrations were highest at the surface, 110 ppm, and uniform in lower sections (averaging 55 ppm), while Ni concentrations were maximal in the 2-5 cm section, 310 ppm, and low (averaging 17 ppm) thereafter.

EIA50: Barium concentrations were considerably lower in all sections of this core, averaging 180 ppm, with the exception of the 2-5 cm section, showing 500 ppm. Zn and Ni concentrations were similar to those found in the E10 core and showed highest concentrations in the surface section, 110 ppm and 33 ppm, respectively. The trace metal patterns were dissimilar to those for hydrocarbons, where maximal values were found at 15-20 cm.

EIA100: The profile for Zn was similar to the total HC profile, with minimal concentrations in the 20-25 cm section, maximal values in the 2-5 cm section and an increase in values in the bottom sections. Barium concentrations did not follow this pattern and appeared to have greater similarity with the pattern for parent PAH, showing maximal values in the surface section and a rise in concentration in the 10-15 cm section. Barium concentrations averaged 150 ppm in sections below the surface, similar to EIA50. Ni concentrations remained low throughout the core, and the average Zn concentration, 57 ppm, was similar to those found in the other cores.

8.5.3 Radionuclides

8.5.3.1 Surficial Sediments

Surficial sediment Pb-210 activities in the Eugene Island study area showed no spatial or temporal trends (Table F.12). Pb-210 activities were approximately the same for both sampling periods and were relatively constant at all stations in the study area. Surface Pb-210 activities ranged from 1.29 to 2.19 dpm g⁻¹ during May 1989 and from 1.68 to 2.69 dpm g⁻¹ during November 1989. Surface sediment Pb-210 activities in coastal environments are typically about 2.0 dpm g⁻¹ (range: 0.1 to 5.0 dpm g⁻¹), depending on many factors controlling the sorption reactions (e.g., grain size, percent organic carbon, turbidity in overlying waters). The surface sediment Pb-210 activities observed at Eugene Island are at or below the upper limit for activities found in natural environments.

8.5.3.2 Vertical Profiles

Sediment Pb-210 activities within the upper 10-50 cm (length of the cores collected) increased or remained the same in a down-core direction (Table F.13). This is different from natural environments where Pb-210 sediment activities decrease down core due to decay and reach a constant background level (~ 0.1 to 0.5 dpm g⁻¹). Decreasing Pb-210 activities with depth in the core is a prerequisite for calculating sedimentation rates; since these conditions were not present, sedimentation rates could not be calculated for Eugene Island (see Section 3.6). The pattern observed at Eugene Island indicated that Pb-210 supply to the sediments had greatly exceeded decay. Because the Pb-210 activities did not decrease to a background level in the Eugene Island cores, the inventories calculated from these cores give a minimum estimate of the Pb-210 flux to the area. During May 1989, the minimum Pb-210 sediment inventories ranged

from 44.6 to 58.9 dpm·cm⁻², representing more than 1.4 to 1.8 times higher Pb-210 supply than natural. During November 1989, the minimum Pb-210 sediment inventories ranged from 56.0 to 66.7 dpm·cm⁻², representing more than 1.7 to 2.1 times higher Pb-210 supply than natural.

8.6 Benthic Biota

Although the Eugene Island study area is located on the inner continental shelf, it is at the terminus of the Atchafalaya River delta and therefore influenced by freshwater runoff and high sedimentation. The benthic macroinfauna was typical of a brackish to intermediate salinity fauna, and composed primarily of polychaetes. The dominant polychaete was the opportunist, *Mediomastus ambiseta*. Other organisms included nemertean worms, oligochaetes, insect larvae, pericaridean crustaceans and a few bivalves and gastropods. While the total number of species for the Eugene Island study site was relatively high, for any single station, the number of species averaged less than 10 per replicate (Table G.17).

The general trend for Eugene Island was reduced numbers of species and individuals of benthic infauna at the discharge point and at some stations near the discharge point (Figure 8.15). Differences among stations were minimal at distances greater than 300 m from the discharge. There were significant differences among stations for some benthic community parameters in both May 1989 and November 1989 (Tables 8.2 - 8.3), as well as a significant interaction of sample date and station for the data combined (Table 8.4). The significance of the interaction, however, was due entirely to the station data and there were no differences due to sample date. In other words, differences seen among stations were real, were related to distance from the discharge and were significant through time. In November 1989 the differences among stations were for more parameters and were stronger than the differences found for the May 1989 benthic data (Tables G.18 - G.19). The combined interaction of station and sample data was significant for all parameters (Table G.20).

In May 1989 Stations E10 and E1A50 were the most obviously impacted (Figure 8.15, Table 8.2). In November 1989 differences extended to 300 m from the discharge point for number of species and to 200 m from the discharge point for number of individuals (Figure 8.15, Table 8.3). The relationship of the stations to each other across time for all community parameters is shown in Table 8.4. While there was some overlap in similarity of stations, there were obvious differences between stations within 250 to 300 m of the discharge compared to those stations at 500 m or greater from the discharge.

Differences in the benthic fauna at Eugene Island were not related to the sediment grain size distribution nor the organic content of the sediments. There were also no seasonal differences between the May high flow period and the November low flow period of the Atchafalaya River.

There were reductions in both the number of species and number of individuals in relationship to certain chemical constituents of the surface sediments. These relationships were stronger for number of individuals than for number of species, but then the species richness for the study area was relatively low. The threshold level for an effect to be seen in the benthic fauna was lower for the number of individuals than for the number of species. The chemical constituents identified are listed in Table 8.5 and some are shown in Figure 8.16.

None of the relationships of chemical constituents were particularly strong, nor were they linear. None were identified in a stepwise multiple regression of environmental parameters important in determining the variation in number of species and individuals. These parameters, however, were non-linear and instead identified threshold levels above which number of species or number of individuals were usually depressed below background levels. There were no

observed threshold levels of chemical constituents in near-bottom waters where levels of volatile and aromatic hydrocarbons were very low.

8.7 Summary

The Eugene Island study area is a shallow, inner continental shelf environment located just offshore of Atchafalaya Bay. The study area receives the discharge of the Atchafalaya River and large volumes of fresh water and sediments. The shallow water depths (2-3 m) allow for wave-generated mixing of the water column, yet the freshwater influence is demonstrated across the 2-km distance of the study site with lowered salinities through the water column or highly stratified waters with a steep salinity gradient. The sediments are predominantly silts which are delivered in the effluent of the Atchafalaya River. Alternating periods of accumulated and resuspended and transported sediments are likely in the study area; however, sedimentation rates could not be calculated because of the high flux of Pb-210 to the area. The shear velocities calculated in May and November indicated that sediment entrainment and transport were likely on both the ebb and flood tides. The study area received a produced water discharge of 21,000 bbl·d⁻¹ of which 100 bbl·d⁻¹ were OCS-generated.

There were no volatile hydrocarbons and PAH detected in the near-bottom waters in May and limited amounts in November within 250 m of the discharge point. Levels of Pb-210 and total radium in near-bottom waters, on the other hand, were elevated above background activities in May and within natural levels in November, with the exception of total radium at a few stations.

Produced water-associated hydrocarbons were evident in surficial sediments to at least 200 m from the discharge point. This was somewhat unexpected given the potential for dilution and dispersion of particulates at this study area. An elevated level of Ba at the central stations with decreases away from the discharge point along both transects followed the same pattern as hydrocarbon contaminants and indicated a similar source. While Pb-210 activities were at or below background levels in surficial levels, the calculations of inventories indicated a general flux of Pb-210 to the study area. Vertical sediment cores indicated that alkylated PAH were accumulated near the surface and to some depth down the core at stations closest to the discharge point. The FFPI values at these same stations indicated a petrogenic hydrocarbon origin. Otherwise, parent PAH dominated the vertical cores to depth and the origin was pyrogenic as indicated by the FFPI values.

Differences in benthic fauna extended to 300 m from the discharge point for number of species and to 200 m for number of individuals. These community changes were related to concentrations of various chemical contaminants.

The results from this study can be compared to the results of Neff et al. (1989) because of similarities in receiving environments, i.e., shallow, open water, and similar chemical analyses. Those discharges were Eugene Island Block 105 platform in 8 m water depth on the inner continental shelf and Lake Pelto Tank Battery No. 1 in 2-3 m water depth in a semi-enclosed bay. Discharge volumes were an order of magnitude less than Eugene Island Block 18 (1,570 bbl·d⁻¹ and 2,750 bbl·d⁻¹, respectively, of 21,000 bbl·d⁻¹). Variation in grain size distribution with distance from the platform complicated the study areas for both Eugene Island Block 105 and Lake Pelto. Sediments were uniform through space and time at Eugene Island Block 18.

At Lake Pelto, sediments out to at least 100 m but not as far as 300 m contained petroleum hydrocarbons, probably derived from produced water discharges. At Eugene Island Block 105, sediments from 20 m contained low concentrations of petroleum hydrocarbons, but sediments from stations farther than 100 m did not contain higher than trace concentrations. By comparison, Eugene Island Block 18 of this study had sediments which were contaminated to a

distance of at least 200 m. The benthic fauna within 20 m of both Eugene Island Block 105 and Lake Pelto were different from those at greater distances. Faunal communities were influenced by both higher petroleum hydrocarbons concentrations as well as sediment grain size differences. By comparison, the benthic fauna of Eugene Island Block 18 in this study was affected to a distance of 250 to 300 m from the discharge. Compared to the two other platforms in shallow open water, the high area of produced water influence at Eugene Island Block 18 was somewhat surprising. The shallow water column at Eugene Island Block 18 and flushing potential of the Atchafalaya River flow were expected to dilute and transport the produced water contaminants. The high silt content and large volume discharge, however, may be factors involved in the larger area of impact.

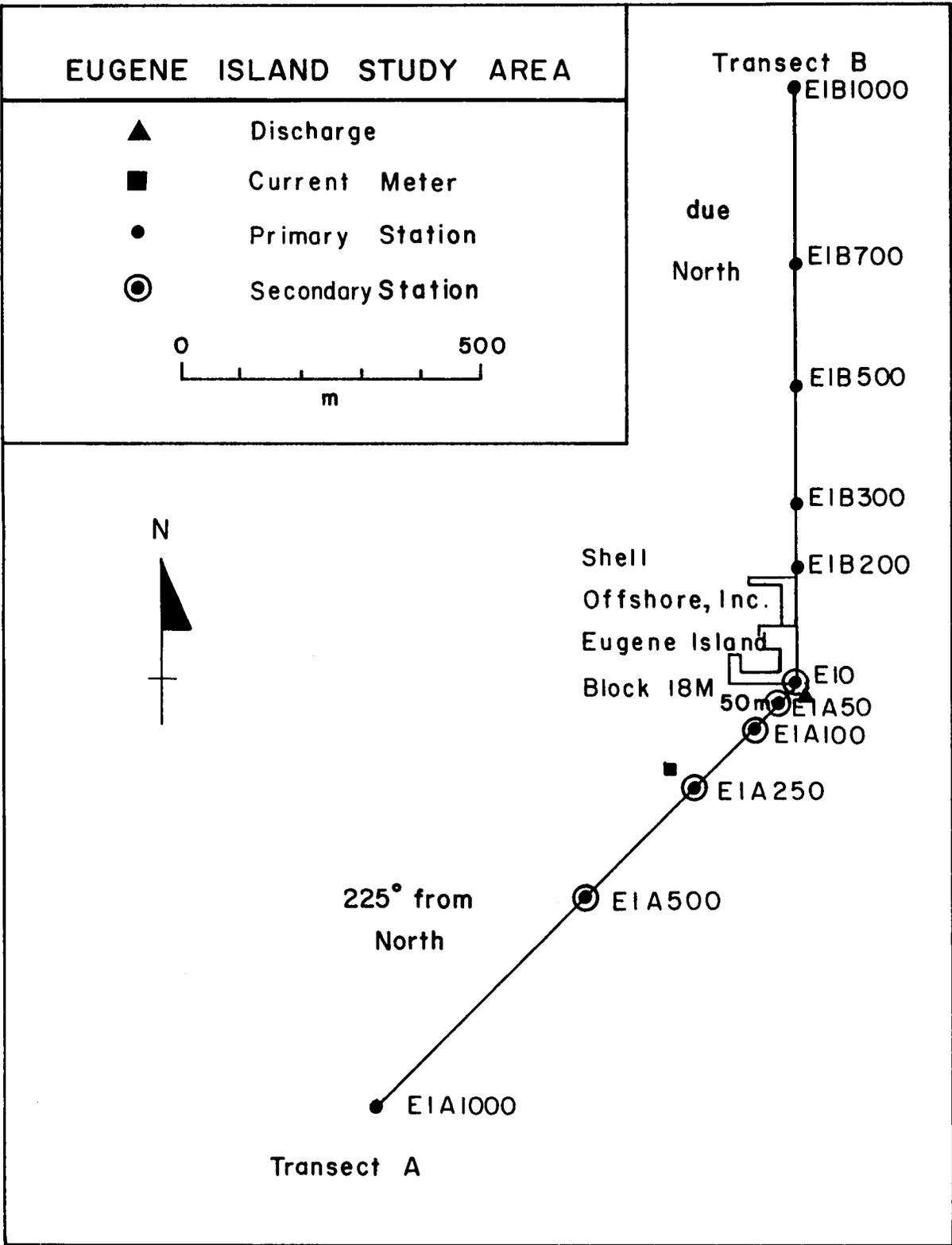


Figure 8.1. Eugene Island Block 18 study area.

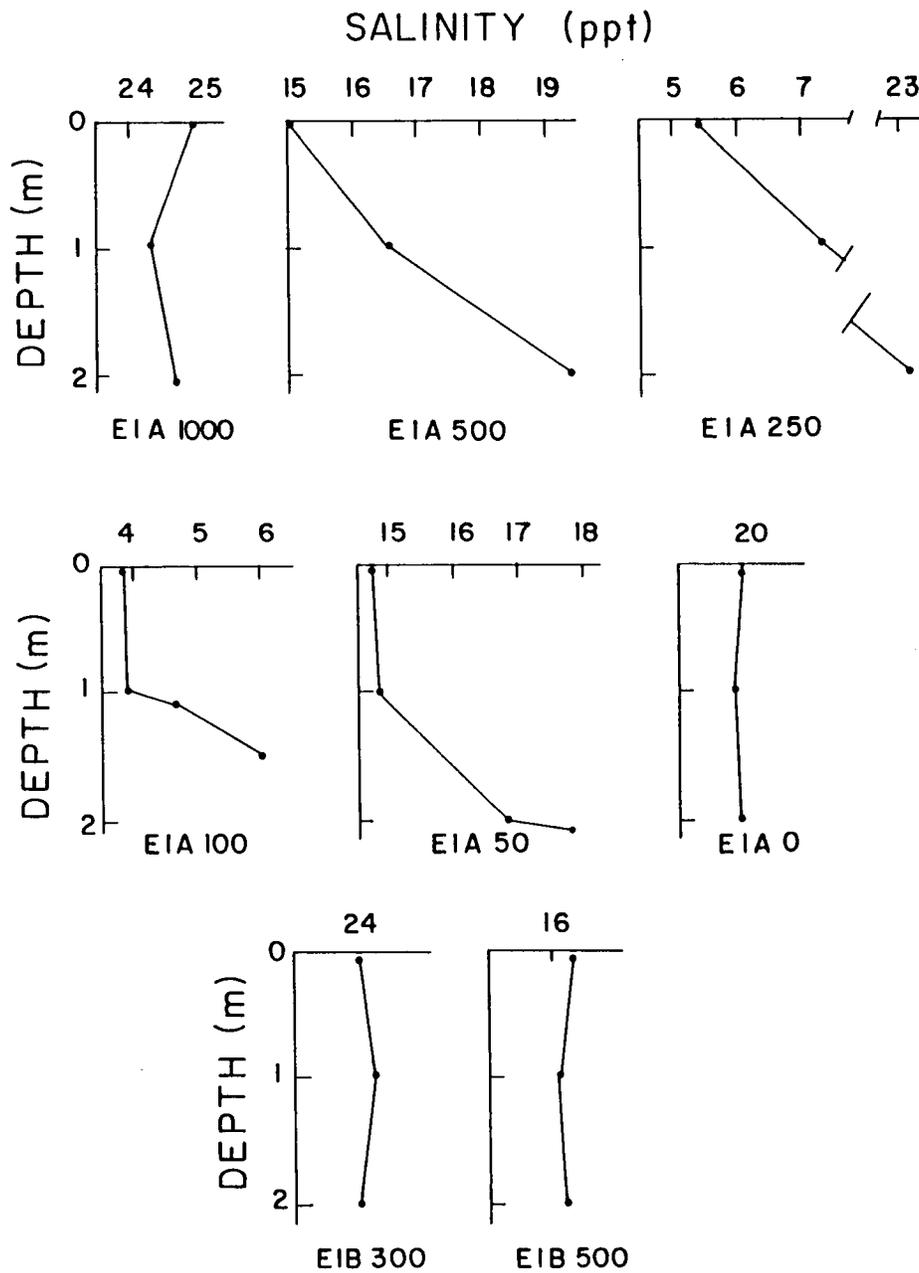


Figure 8.2. Salinity distribution through the water column at selected stations for Eugene Island, May 1989.

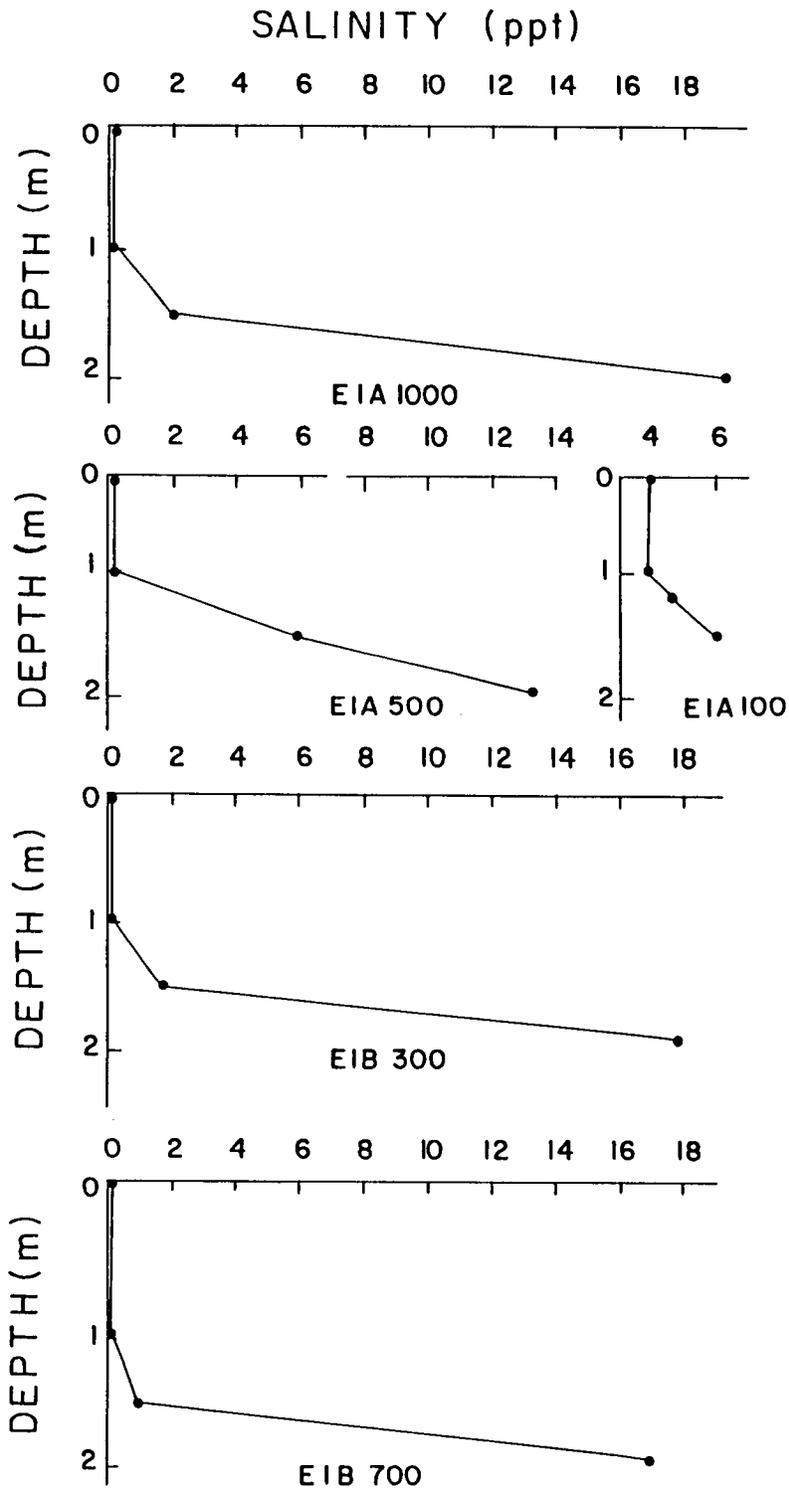


Figure 8.3. Salinity distribution through the water column at selected stations for Eugene Island, November 1989.

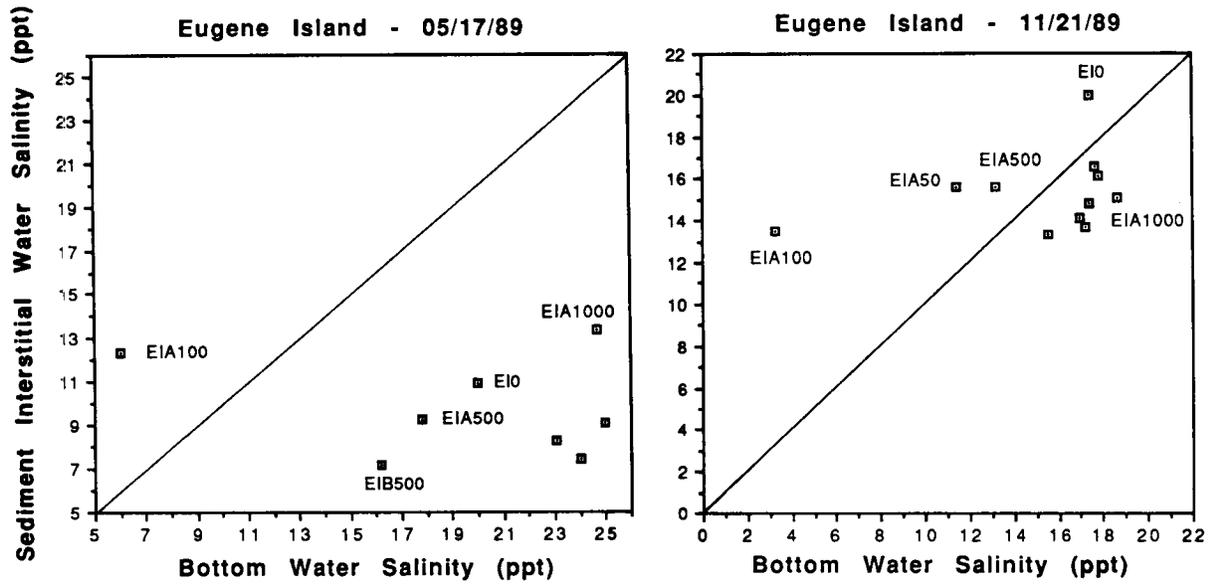


Figure 8.4. Comparisons of interstitial water salinity from surface sediments of stations in the Eugene Island study area and near-bottom water salinity. Station number given for values most different from a 1:1 relationship (indicated by diagonal line).

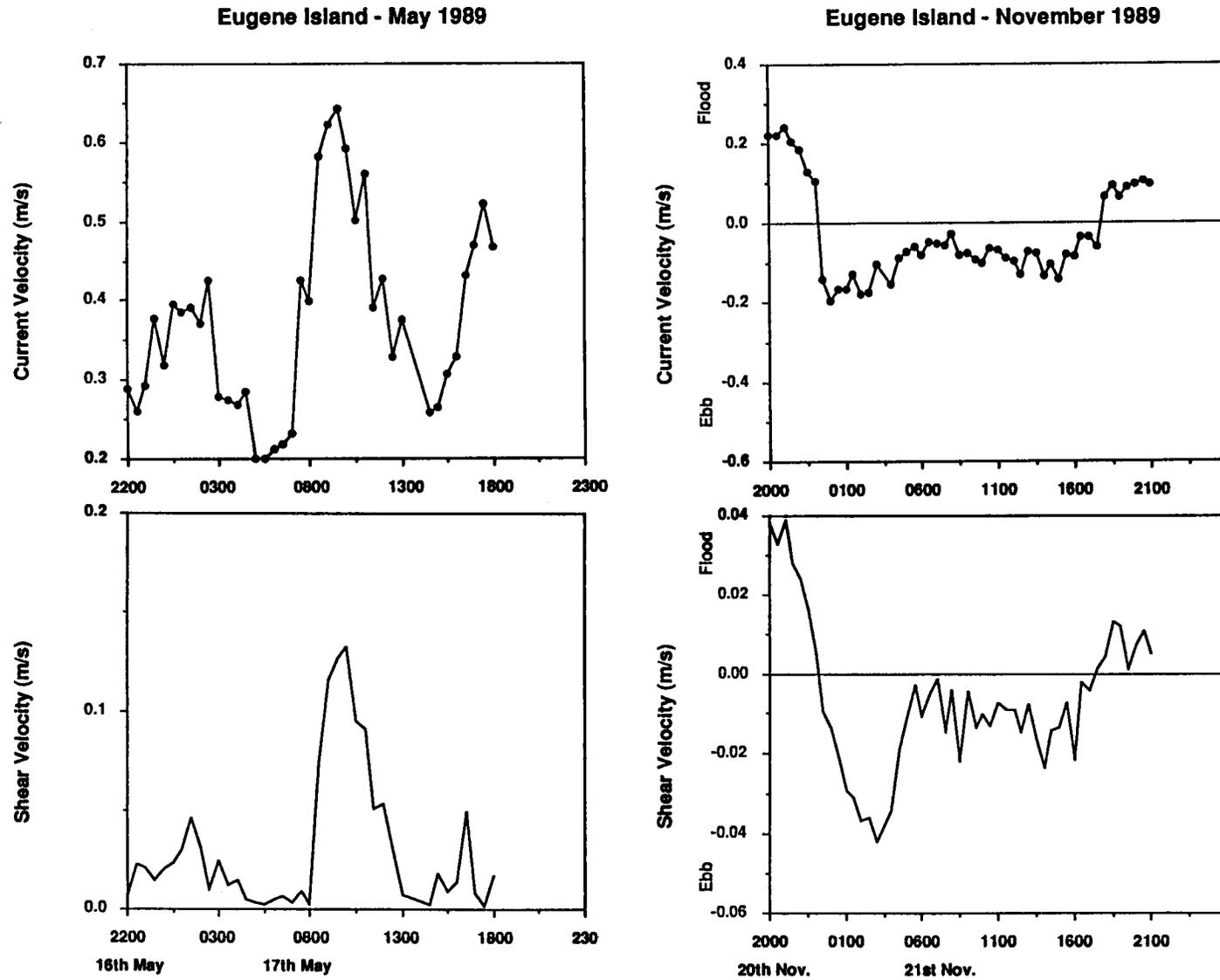


Figure 8.5. Mean tidal current velocity variation and calculated shear velocities for Eugene Island, May and November 1989.

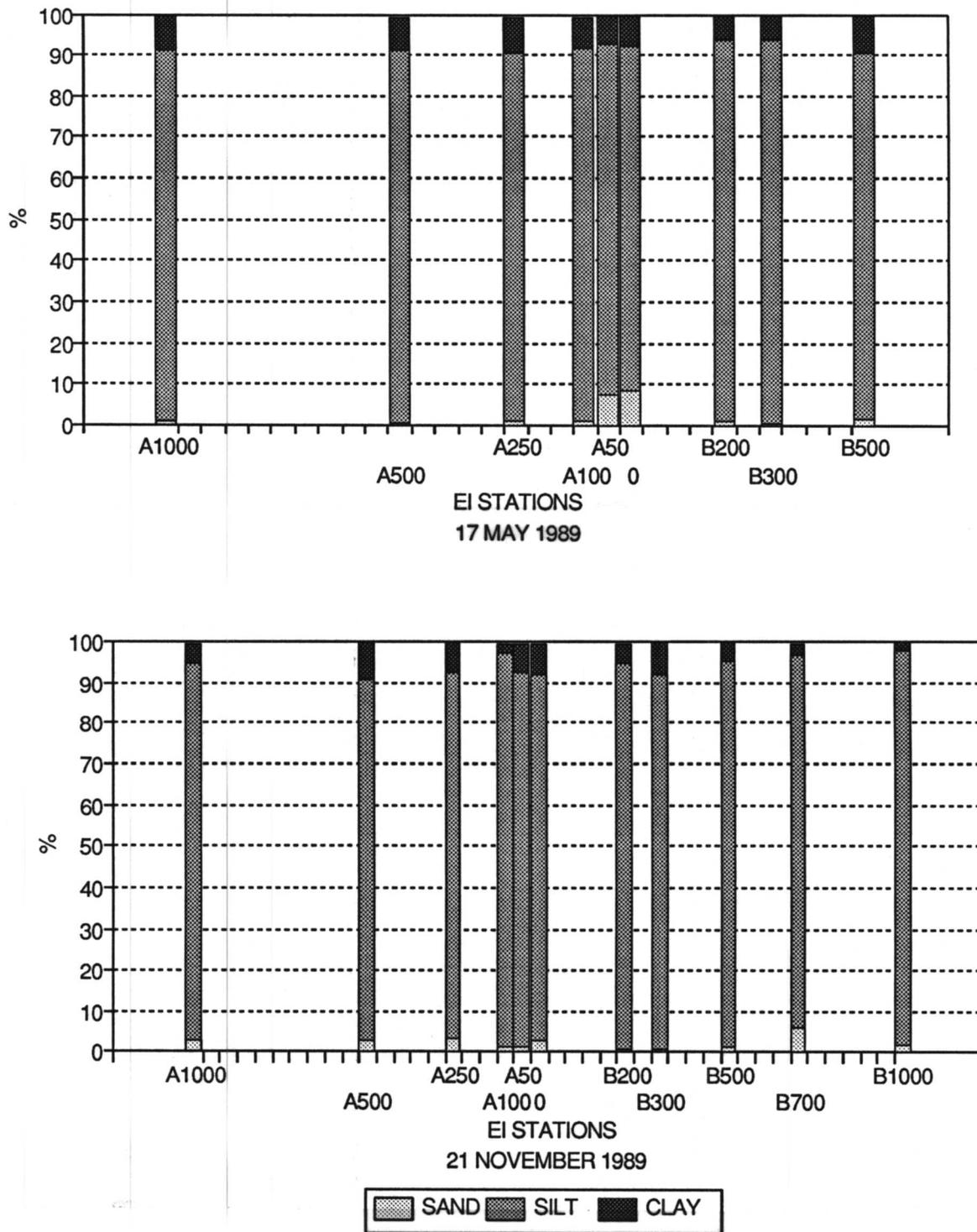


Figure 8.6. Spatial distribution of surface sediment grain size from Eugene Island for two sample periods.

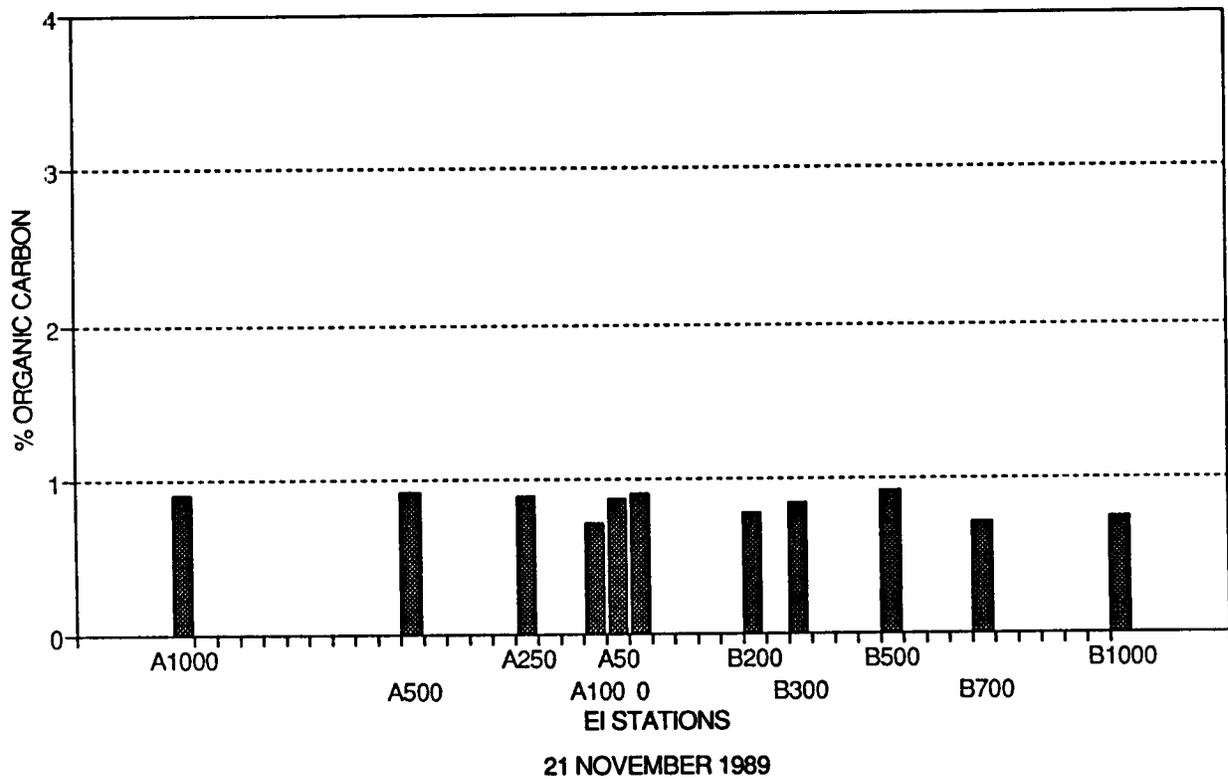
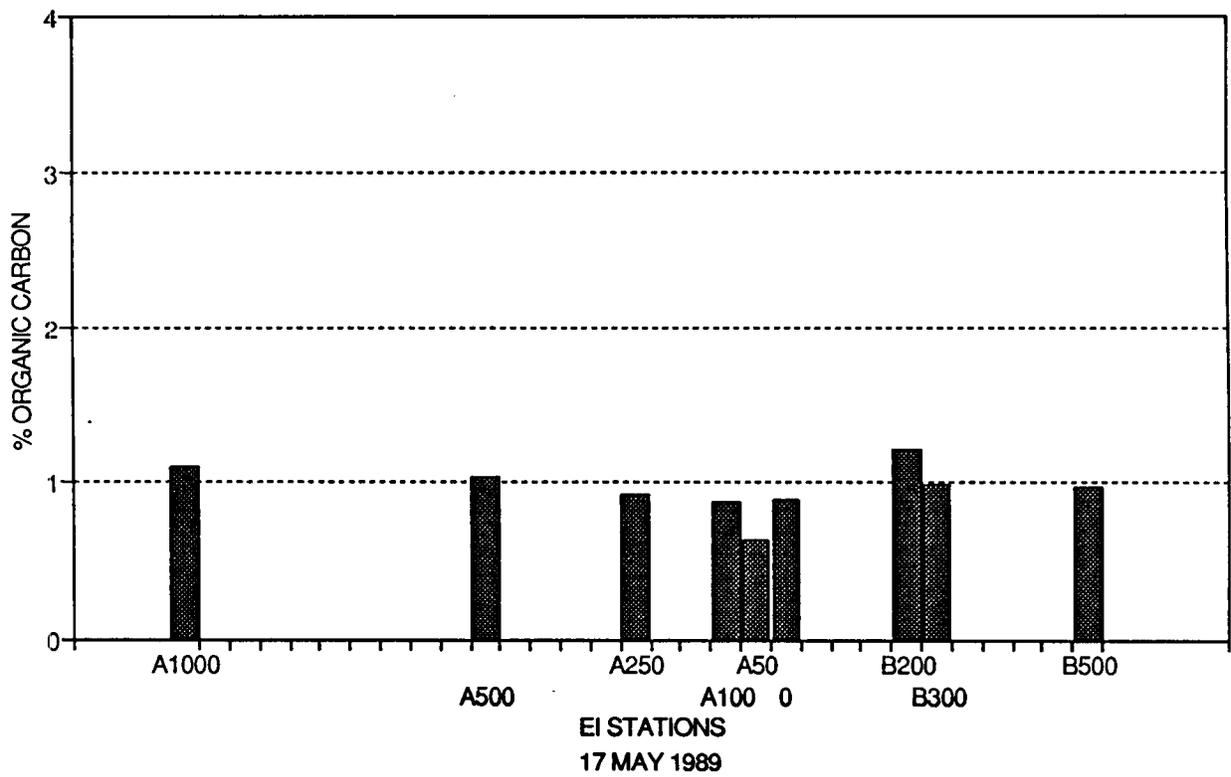


Figure 8.7. Spatial distribution of percent total organic carbon in surface sediments from Eugene Island for two sample periods.

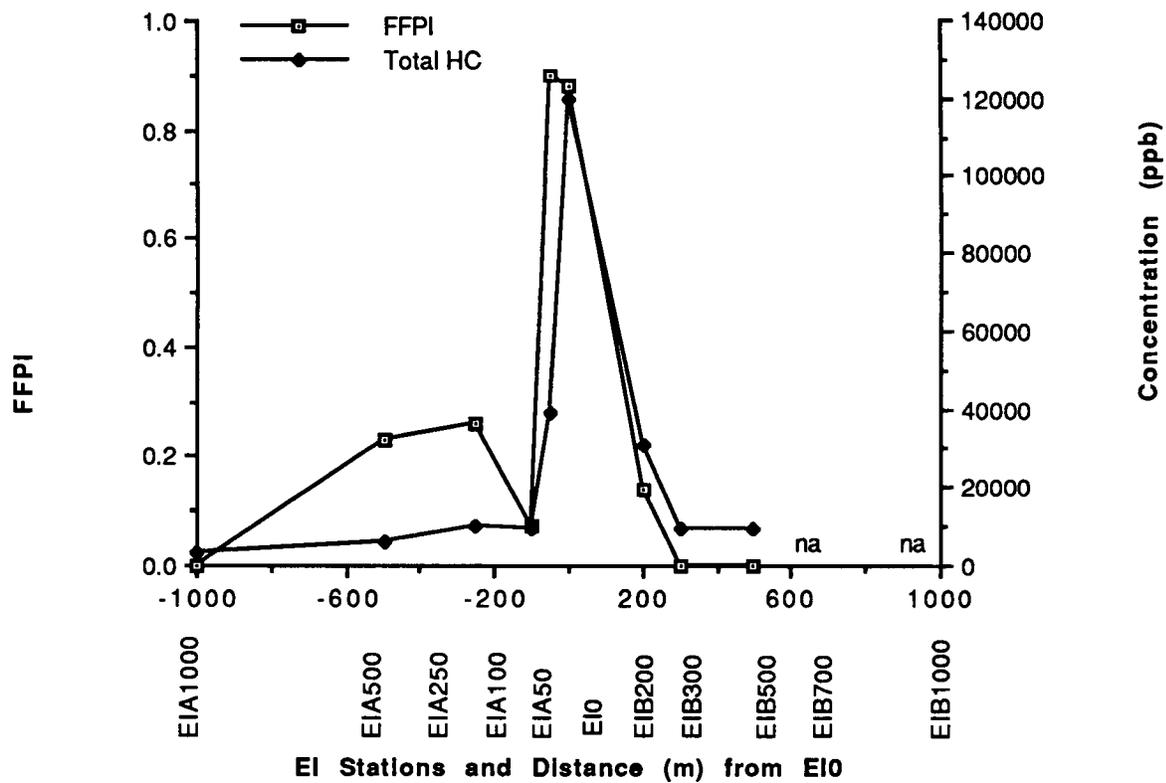
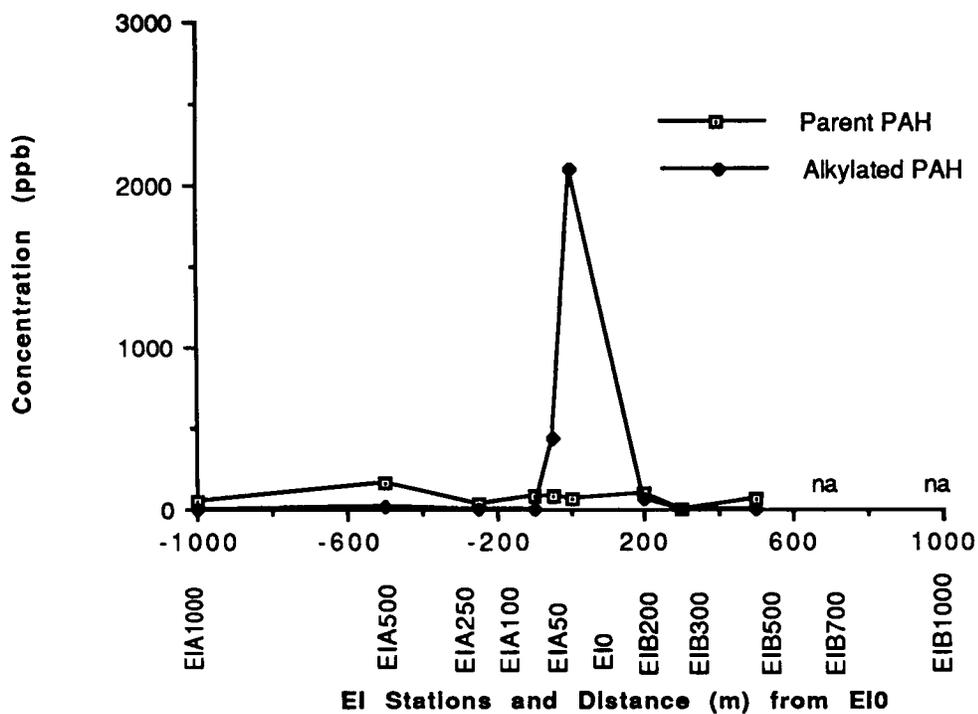


Figure 8.8. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from Eugene Island, May 1989.

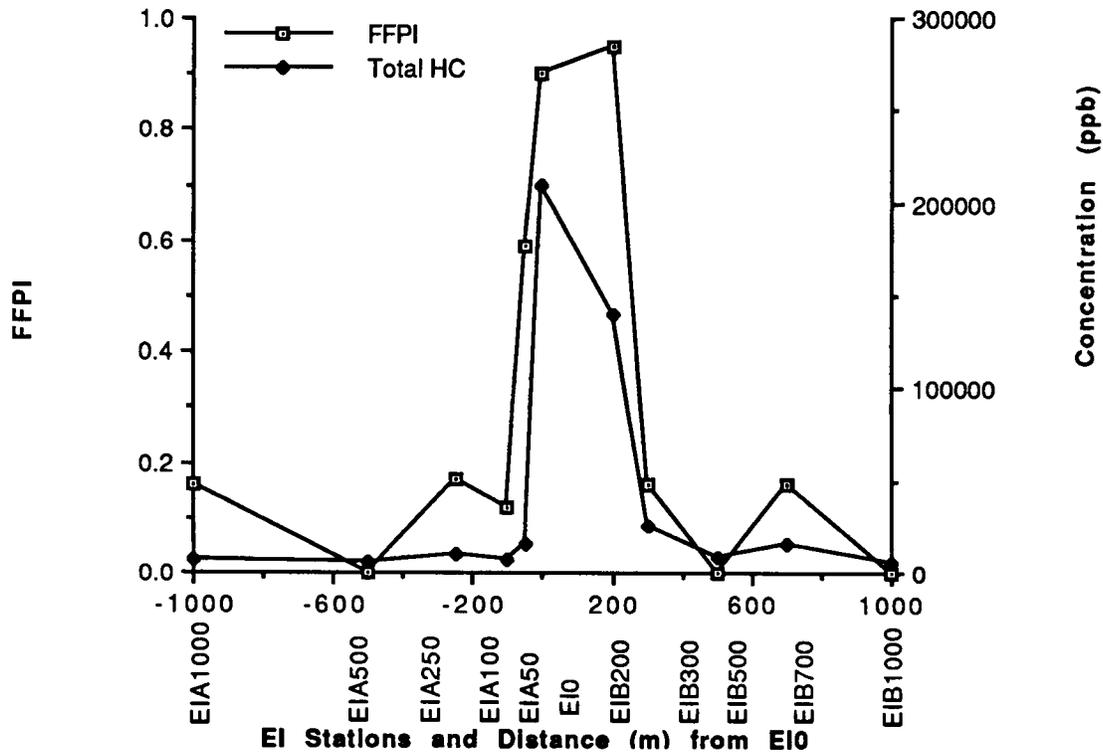
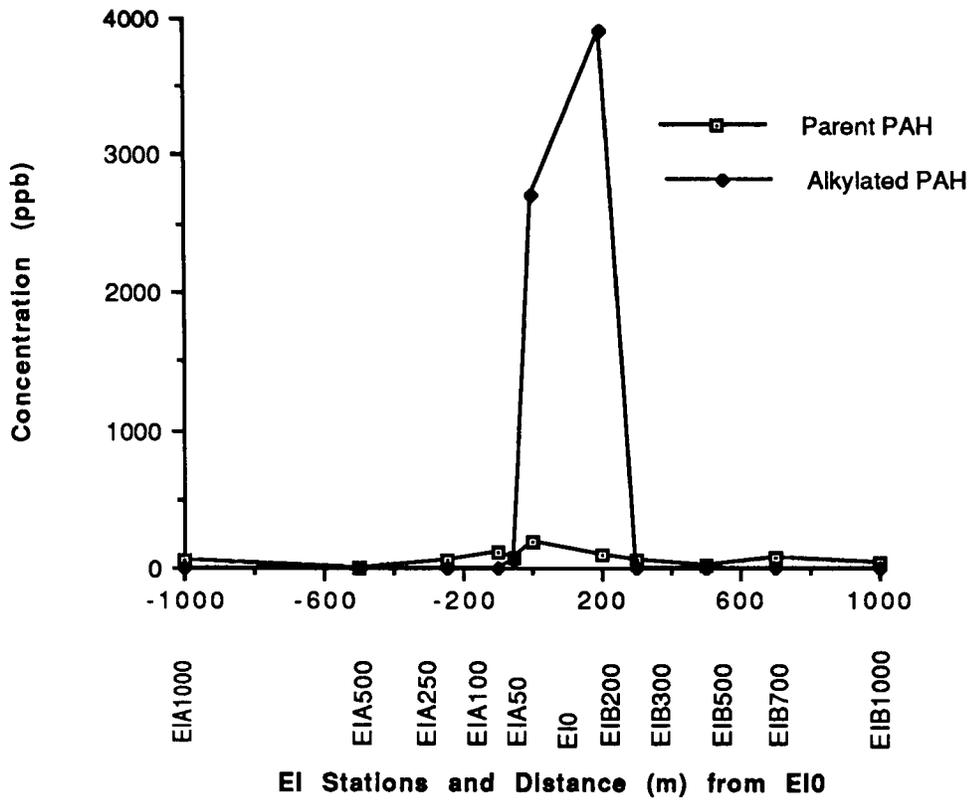


Figure 8.9. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from Eugene Island, November 1989.

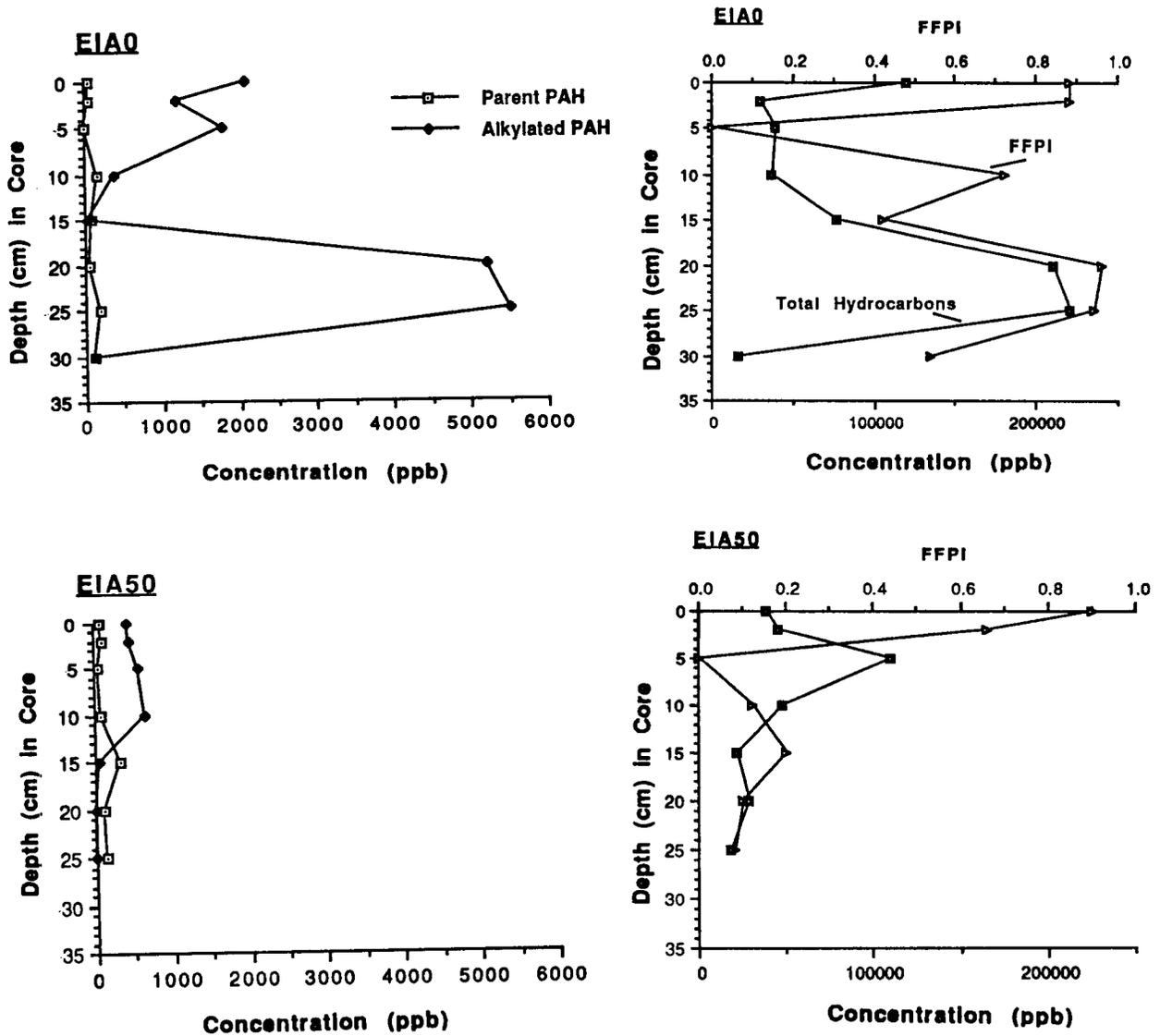


Figure 8.10. Total parent and alkylated PAH concentrations, FFPI and total HC concentrations in vertical sediment core sections from selected stations at Eugene Island, May 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

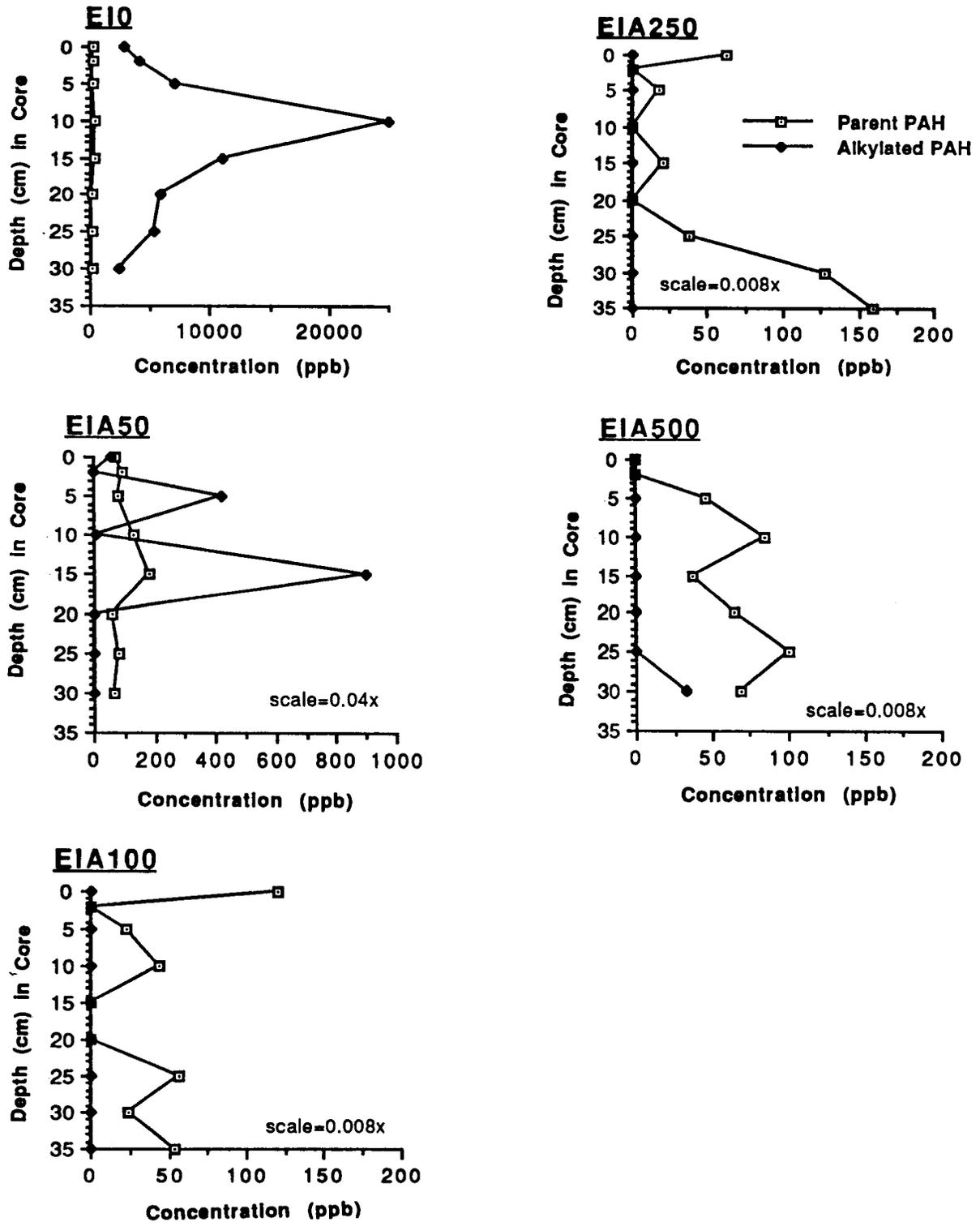


Figure 8.11. Total parent and alkylated PAH concentrations in vertical sediment core sections from Eugene Island, November 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

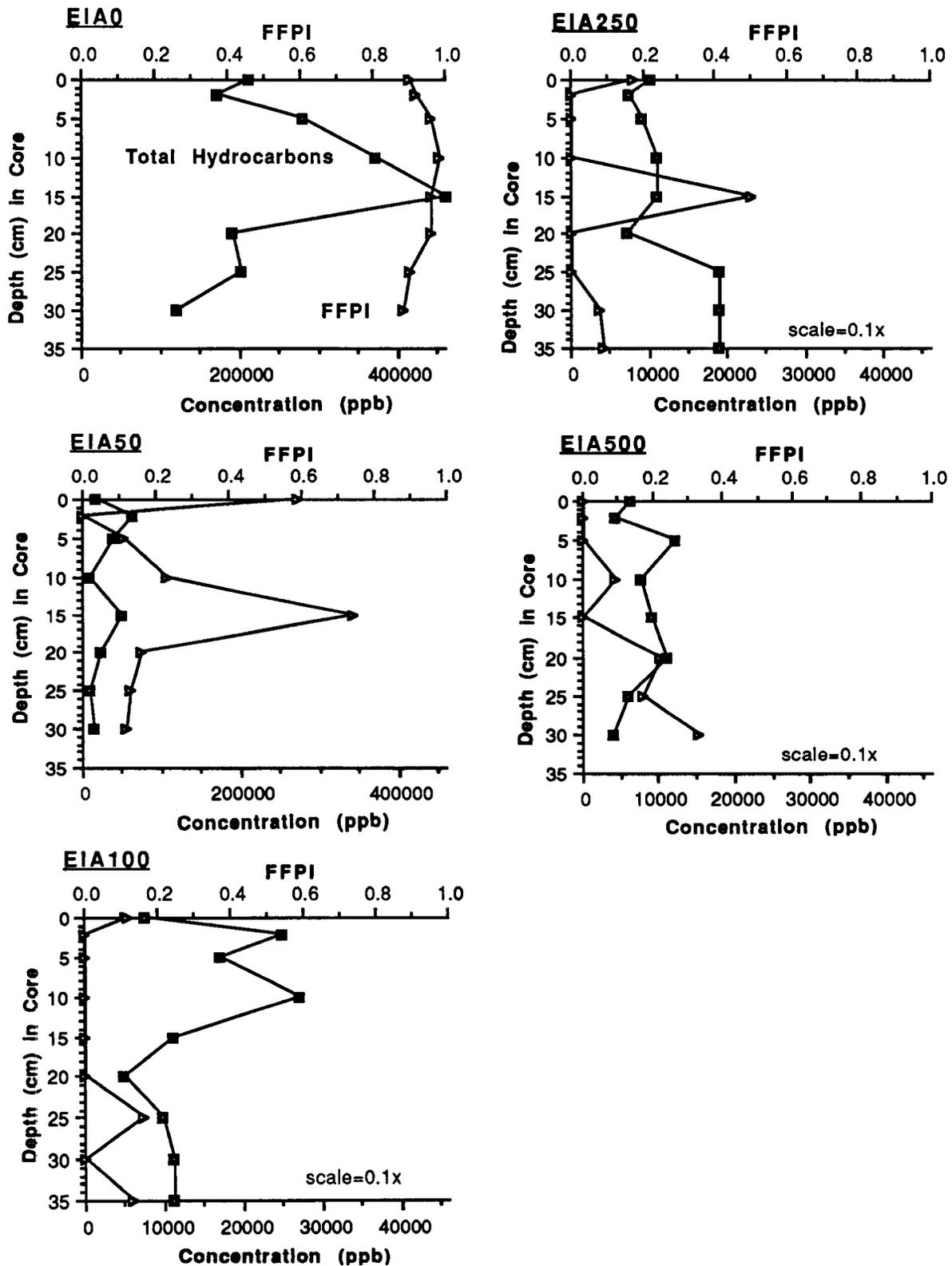


Figure 8.12. FFPI and total HC concentrations in vertical sediment core sections from selected stations at Eugene Island, November 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

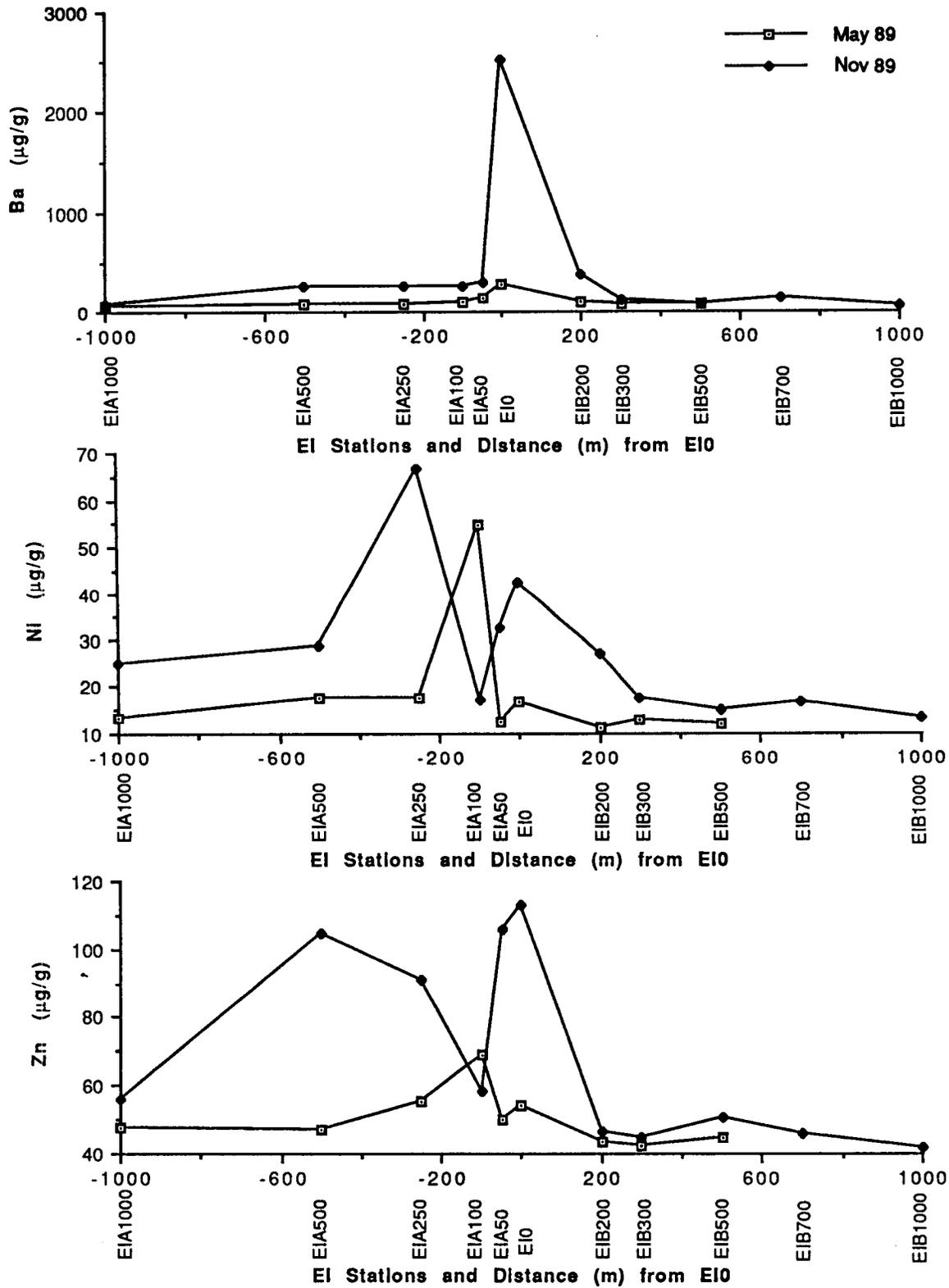


Figure 8.13. Spatial distribution of selected trace metal concentrations in surface sediments from Eugene Island for two sample periods.

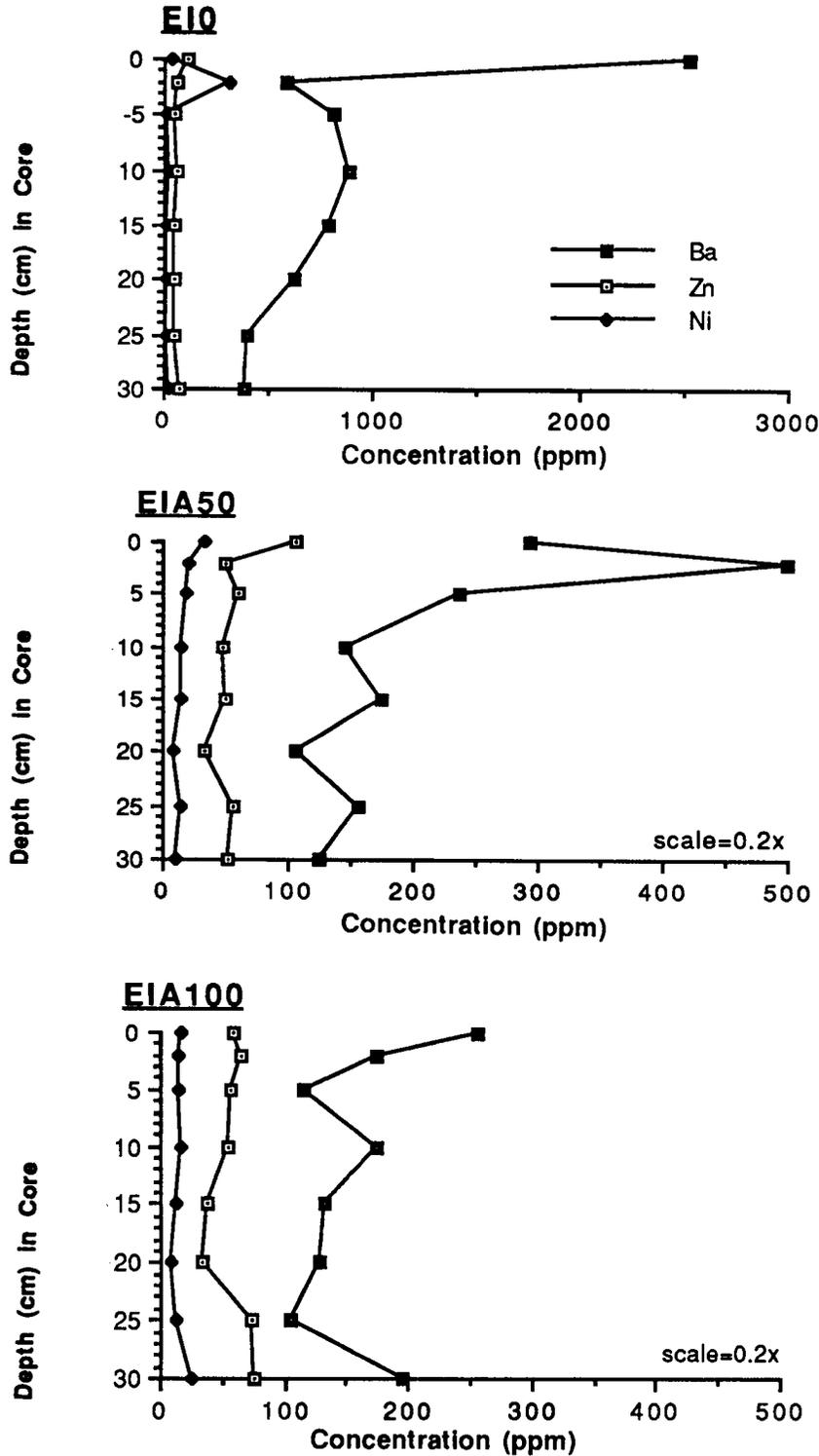


Figure 8.14. Selected trace metal concentrations in vertical sediment core sections from selected stations at Eugene Island, November 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

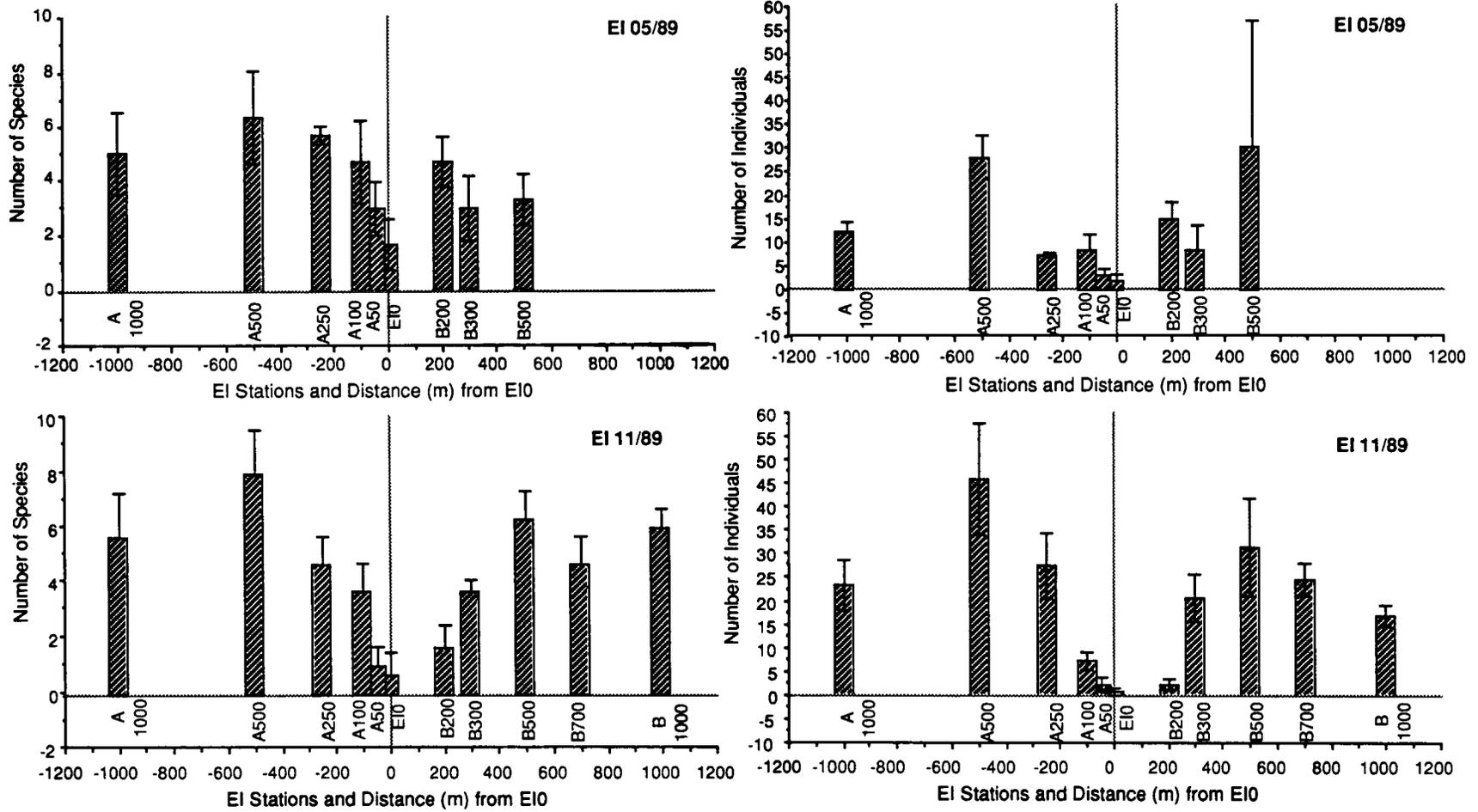


Figure 8.15. Spatial distribution of number of species per replicate (mean + standard error) and number of individuals per replicate (mean + standard error) for Eugene Island for two sample periods.

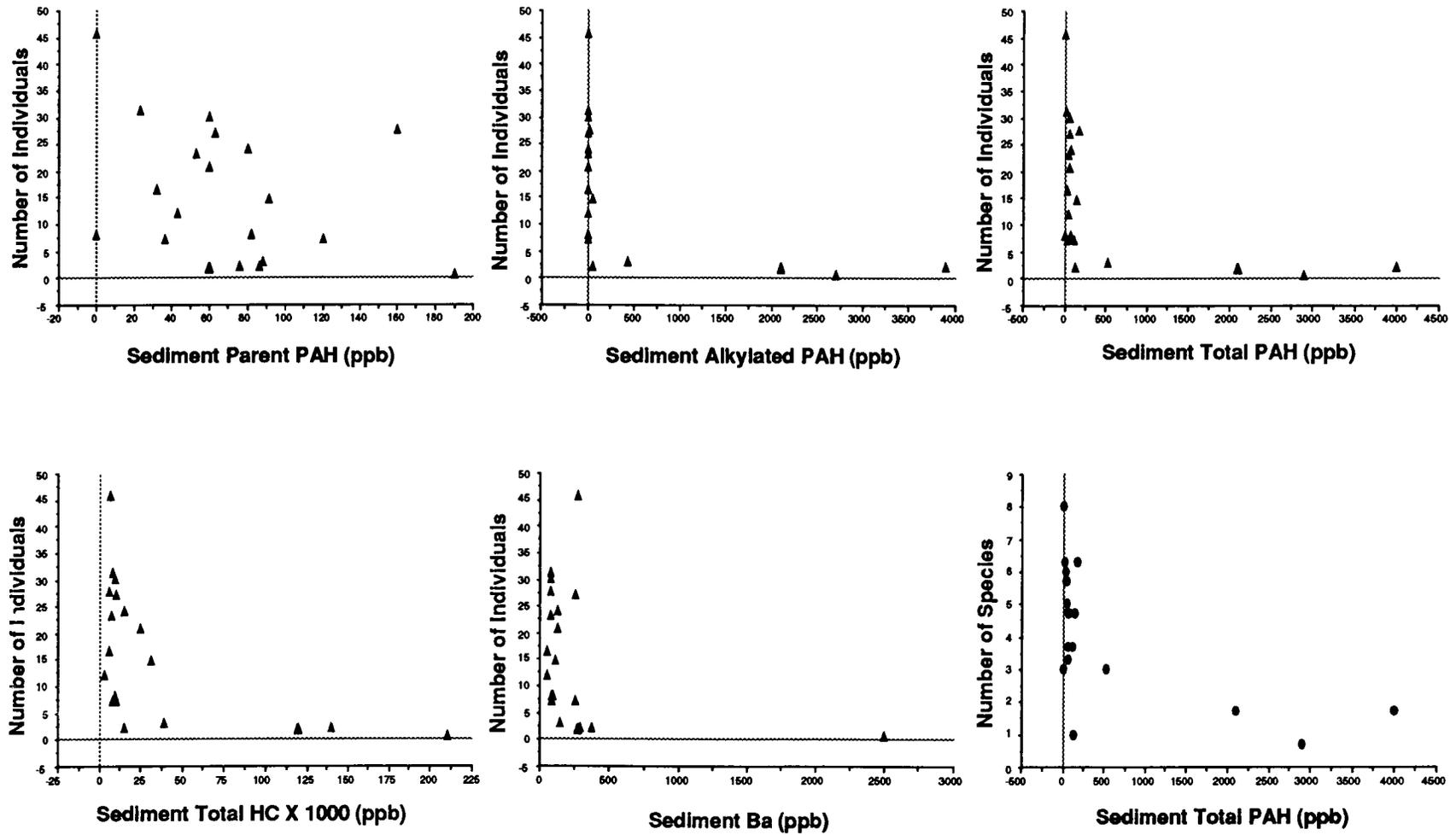


Figure 8.16. Relationship of mean number of species per replicate and mean number of individuals per replicate to various sediment contaminants for Eugene Island for all sample periods combined.

Table 8.1. Average daily discharge (bbl·d⁻¹) and oil and grease content (mg·l⁻¹) of produced waters from facility at Eugene Island Block 18 study area. (Data provided by operator.)

Date	Facility
	Eugene Island Block 18M
05/89	
Discharge	24,000
Oil and Grease	11
11/89	
Discharge	21,000
Oil and Grease	14
Average Discharge	21,000*
Average Oil and Grease	18*

*Mean of 25 monthly sample dates from 01/88 - 01/90.

Table 8.2. Duncan's multiple range test for Eugene Island study area, May 1989; underlined stations are not significantly different from each other.

Number of Species (natural log transformed):

500	200	500	1000	250	100	300	50	0
<u>A</u>	<u>B</u>	<u>B</u>	<u>A</u>	<u>A</u>	<u>A</u>	<u>B</u>	<u>A</u>	

* Evenness (J'):

50	0	250	100	1000	500	300	200	500
<u>A</u>		<u>A</u>	<u>A</u>	<u>A</u>	<u>B</u>	<u>B</u>	<u>B</u>	<u>A</u>

Table 8.3. Duncan's multiple range test for Eugene Island study area, November 1989; underlined stations are not significantly different from each other.

Number of Species:

500	500	1000	1000	250	700	100	300	200	50	0
<u>A</u>	<u>B</u>	<u>B</u>	<u>A</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>B</u>	<u>A</u>	

Number of Individuals (natural log transformed):

500	500	250	700	1000	300	1000	100	200	50	0
<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	

* Diversity (H')

1000	1000	500	500	100	700	250	300	0	200	50
<u>B</u>	<u>A</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>		<u>B</u>	<u>A</u>

* Cell sizes unequal due to missing values.

Table 8.4. Duncan's multiple range test for Eugene Island study area, both sample periods combined for nine stations; underlined stations are not significantly different from each other.

Number of Species:

500 A	1000 A	250 A	500 B	100 A	300 B	200 B	50 A	0
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Number of Individuals:

500 A	500 B	1000 A	250 A	300 B	100 A	200 B	50 A	0
----------	----------	-----------	----------	----------	----------	----------	---------	---

* Diversity (H'):

1000 A	250 A	100 A	500 A	500 B	0	50 A	200 B	300 B
-----------	----------	----------	----------	----------	---	---------	----------	----------

* Evenness (J'):

0	50 A	100 A	1000 A	250 A	200 B	500 B	300 B	500 A
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* Cell sizes unequal due to missing values.

Table 8.5. Concentrations of various chemical constituents in surficial sediments at Eugene Island at or above which there was a depressed benthic fauna (N/A = not applicable).

Chemical Constituent	Number of Species	Number of Individuals
Surficial Sediments:		
Parent PAH ($\mu\text{g}\cdot\text{g}^{-1}$)	N/A	190
Alkylated PAH ($\mu\text{g}\cdot\text{g}^{-1}$)	430	430
Total PAH ($\mu\text{g}\cdot\text{g}^{-1}$)	2,100	520
Total Saturated HC ($\mu\text{g}\cdot\text{g}^{-1}$)	31,000	31,000
Barium ($\mu\text{g}\cdot\text{g}^{-1}$)	500	370
Aluminum ($\mu\text{g}\cdot\text{g}^{-1}$)	N/A	12,000

Chapter 9

EAST TIMBALIER ISLAND STUDY AREA

9.1 Description of Study Area

9.1.1 Facilities

Numerous discharges handling OCS-generated produced waters as well as those generated within the State's territorial sea and estuarine waters are located in and near the East Timbalier Island study area (Table 9.1). Two facilities handling OCS produced waters during our study were Chevron U.S.A. Inc.'s Tank Battery 21, 27, 28 (discharge T-1) and Tank Battery 36, 37 (discharge T-2). Another OCS-generated discharge at Tank Battery 35 was discontinued since the Boesch and Rabalais (1989a) study and the initiation of this study in October 1988. Additional discharges at Tank Battery 2 and Tank Battery 3 are generated within State waters.

All discharges are located within a complex of dredged access canals and natural water bodies on the back barrier side of East Timbalier Island along the southern edge of Timbalier Bay (Figure 9.1). The ambient salinities at the time of sample collections were 23 to 24 ppt. The water column is shallow (1.5 to 2 m) and well-mixed. Where the access canals dead-end into the back barrier side of East Timbalier Island, tidal currents are sluggish. On the northern edge of the study site along the southern end of Timbalier Bay the water column is influenced more by tidal currents and the wind mixing of the open bay waters. Vegetation in the area is typical salt marsh vegetation, *Spartina alterniflora*.

The volumes, activities, operators and status of the discharges in the East Timbalier Island study area have been in constant flux since 1988. During the field studies of the Boesch and Rabalais (1989a) study, there were five active discharges (3 OCS and 2 State) for a combined total discharge volume to the immediate study area of 21,621 bbl·d⁻¹. During the field studies of this project, there were four active discharges (2 OCS and 2 State) for a combined total discharge volume of 25,558 bbl·d⁻¹. Currently (as of 03/91), there are three active discharges (1 OCS and 2 State) for a combined volume of 15,795 bbl·d⁻¹.

The produced water discharges at the East Timbalier Island study area (Figure 9.1) are identified as follows:

T-1 is the Chevron U.S.A. Inc. discharge from Tank Battery 21, 27, 28. The facility was installed pre-1960 and had been producing continuously, except short periods of down-time, until the product stream was completely rerouted prior to March 1991. The average discharge rate for the facility was 13,258 bbl·d⁻¹ with a stable rate of discharge over 25 months from February 1988 - February 1990 (Table 9.1). The hydrocarbon levels of the discharge, reported as oil and grease content, averaged 24 mg·l⁻¹ over the same 25-month period. The reported salinity of the discharge was 86.5 ppt chloride (156 ppt salinity). Company representatives indicated that there were no known treatment technologies which should significantly alter the chemical analyses.

T-2 is the Chevron U.S.A. Inc. discharge from Tank Battery 36, 37. The facility was installed pre-1960 and has been producing continuously, except short periods of down-time. The average daily discharge rate for the facility was 5,005 bbl·d⁻¹ with a stable rate of discharge over 25 months from February 1988 - February 1990 (Table 9.1). The hydrocarbon levels of the discharge, reported as oil and grease content, averaged 20 mg·l⁻¹ over the same 25-month period. The reported salinity of the discharge was 104 ppt chloride (187 ppt salinity). Company

representatives indicated that there were no known treatment technologies which should significantly alter the chemical analyses.

Chevron U.S.A. Inc.'s Tank Battery 35 (TB 35) discharged an average of 5,672 bbl d^{-1} until October 1988 when the discharge was discontinued (Table 9.1). The facility had been producing continuously, except for short shut-down periods, since pre-1960 when the facility was installed. Prior to cessation of the discharge, the hydrocarbon levels of the discharge, reported as oil and grease content, averaged 17 $\text{mg}\cdot\text{l}^{-1}$ and the salinity averaged 88.3 ppt chloride (159 ppt salinity). Tank Battery 35 has since been sold to another operator.

Chevron U.S.A. Inc.'s Tank Battery 2 (TB 2) discharged an average of 4,866 bbl d^{-1} over a 25-month period from February 1988 - February 1990 (Table 9.1). The hydrocarbon levels of the discharge, reported as oil and grease content, averaged 19 $\text{mg}\cdot\text{l}^{-1}$ over the same 25-month period. The reported salinity of the discharge was 110 ppt chloride (198 ppt salinity). Tank Battery 2 has since been sold to another operator.

Chevron U.S.A. Inc.'s Tank Battery 3 (TB 3) discharged an average of 2,429 bbl d^{-1} over the 25-month period from February 1988 - February 1990 (Table 9.1), with a 2-month interruption in service in early 1988. The hydrocarbon levels of the discharge, reported as oil and grease content, averaged 21 $\text{mg}\cdot\text{l}^{-1}$ over the same 25-month period. Salinity data were not available. This facility was sold to another operator early in 1990.

9.1.2 Study Design

A series of stations were situated along a north-south access canal into East Timbalier Island and along an east-west transect on the island's northern shoreline (Figure 9.1). Stations were located adjacent to discharge sites (either active or discontinued) and at similar distances away from the discharges. Fifteen stations were sampled a single time in May 1989. Some of the stations could be accessed from the R/V *Acadiana*, others only from a small boat. Because of vessel limitations, only surficial sediments, and not vertical cores, were collected. Near-bottom water samples were collected from some of the stations. The current meter station was a small boat anchor station located near station T9.

The data for the East Timbalier Island study area are plotted on two transects as a function of distance from a single discharge on each transect. On the east-west transect, the focus was Tank Battery 36, 37 (T-2) at station T12. On the north-south transect, the focus was Tank Battery 21, 27, 28 (T-1) at station T4. Station T9 was common to both transects for intercomparison and occupied the position of -290 m in the east-west transect and +580 m in the north-south transect.

9.2 Hydrography

9.2.1 Hydrographic Profiles

The water column is shallow at all stations for the East Timbalier Island study area. The deepest station was T14 (2.1 m), and all others were less than 1 or 2 m deep. The salinity profiles were well-mixed with values of 22 to 24 ppt, with the exception of station T3 (Figure 9.2, Table A.13). At station T3 there was a steep increase in salinity below 0.5 m to 38 ppt at 1 m.

Water temperatures were near 25°C for all stations for all depths. The water column at most stations was well-oxygenated. At T3 the bottom water was reduced in dissolved oxygen (3.3 $\text{mg}\cdot\text{l}^{-1}$), but the levels are not considered deficient (< 2 $\text{mg}\cdot\text{l}^{-1}$). Sulfide concentrations were not measured.

9.2.2 Dispersion of Effluent

The average salinity for the produced water discharges collected from the East Timbalier Island study site was 156 ppt. Other than the increased bottom water salinity at station T3, there was no evidence of an effluent density plume for the produced water discharges. Station T3 is located next to a produced water discharge in a dead-end canal to where the brine effluent likely is moved and accumulated.

The interstitial salinity of surficial sediments at station T3 were elevated but consistent with the high salinity of the near-bottom water (Figure 9.3). The elevated salinity of interstitial waters in surficial sediments at T6 indicated prior exposure to higher salinities than detected on the day of sampling. The same was true for other stations where interstitial salinities of > 27 ppt were found. Higher interstitial salinities at these stations may indicate prior exposure to higher salinities from a produced water effluent.

9.2.3 Tidal Current Regime

Tidal currents were monitored for 25 hours at an anchor station 50 m south of station T9 in approximately 1.5 m of water. Both flood and ebb tidal flows were identified (Figure 9.4). There was considerable variation in the magnitude of the mean velocity with flood generally being stronger than ebb. Flood velocities reached $0.2 \text{ m}\cdot\text{s}^{-1}$, although not for sustained periods, and ebb velocities were typically less than $0.1 \text{ m}\cdot\text{s}^{-1}$.

The ebb flow, however, was of longer duration than the flood. The complex pattern of channels and canals at East Timbalier could account for these variations. The canal in which the current monitoring took place could be a main flood channel while other canals may channel most of the ebb flow. Further investigations of flow through the back barrier marshes of East Timbalier Island would be required to explain the variation between flood and ebb flows found during this study.

9.2.4 Velocity Profiles

The velocity profile data for East Timbalier were variable in slope. Shear velocities showed some high peaks on the flood tide (Figure 9.4). The ebb tide also showed variation but of a lesser magnitude. During the peaks, or pulses of velocity on the flood, sediment may be entrained at the bed. The high bed shear stress, however, was of short duration and would not, therefore, result in the transport of large volumes of material. Higher shear velocities on the flood, i.e. south towards the back of the island, may result in net sediment transport into the canal. This will depend upon the grain size of sediment available for entrainment and the magnitude and duration of the flood and ebb shear stress.

9.3 Water Column Contaminants

9.3.1 Hydrocarbons

The data for near-bottom water are presented in Table D.13. The majority of samples had no detectable levels of volatiles or PAH. Water from station T4, which is adjacent to a discharge source (T-1), contained low levels of volatile hydrocarbons and trace levels of naphthalenes. Volatiles and trace levels of PAH were detected in water from T6, which is opposite TB 35, a discontinued produced water source. The low levels of volatiles and PAH in this study area were found only in near-bottom water samples in the immediate vicinity of a produced water discharge (station T4) or within 250 m (station T6).

9.3.2 Radionuclides

Pb-210: Pb-210 activities in near-bottom waters were highest at station T7 (about mid-way between the two discharge points) with an activity of $0.51 \text{ dpm}\cdot\text{l}^{-1}$, about 5 times greater than natural levels (Figure 9.5, Table F.4). Pb-210 activities elsewhere in the study area were lower, all within the range of natural activities.

Radium: In all water samples, U-238 and Th-234 activities were below detection levels (<0.5 and $<0.8 \text{ dpm}\cdot\text{l}^{-1}$, respectively). This lack of enhanced uranium and thorium activity indicates strongly that the high radioactivity levels associated with produced waters originate with the radium isotopes and is not supported by radioactive parents of radium which are higher in the decay chain. Total radium is the sum of Ra-226 and Ra-228 activities. The ratio of Ra-226/total Ra varies from site to site for produced waters, but in most cases the Ra-226 activity constitutes more than two-thirds of the total radium activity.

Water column total radium activities in near-bottom waters were highest at station T7 (about mid-way between the two discharge points) with an activity of $89 \text{ dpm}\cdot\text{l}^{-1}$, about 45 times greater than natural levels (Table F.4). Total radium activities elsewhere in the study area were relatively uniform (range: 32 to $55 \text{ dpm}\cdot\text{l}^{-1}$). Total radium levels within the study area were 15 to 45 times natural activities.

9.4 Sedimentary Characteristics

9.4.1 Grain Size Distribution

Grain size distributions were used to broadly distinguish two zones in the East Timbalier Island study area. Stations T1 - T8 were $>80\%$ sand with $<2\%$ clay, whereas stations T9 - T15 showed an increased silt and clay content to $>20\%$ of the total (Figure 9.6, Table B.1). The exception was T13 which is in shallow water, west of the main east-west oriented channel through the back barrier marshes. It is more readily grouped with T1 - T8 which are in the north-south oriented channel from the back of the island towards the beach. Overwash sands introduced into this channel from the sandy shoreline during storm events may account for the increased percentage of sand in the north-south channel.

9.4.2 Total Organic Carbon (TOC)

The TOC content of surface sediment samples at East Timbalier was less than 1% for all samples (Figure 9.7, Table B.1). Lowest values were found at stations T1, T2, T4 and T5 which were in the area closest to the barrier beach environment and which had high sand contents. Examining the relationship between TOC content and grain size data using regression analysis showed a significant negative relationship (at $P=0.05$) between percent sand and percent TOC (Figure 9.8). Variations in TOC content were accounted for by variations in fine sediment content, and the spatial pattern of TOC values was associated with the sedimentological characteristics of the various back barrier channels and canals.

9.5 Sediment Contaminants

9.5.1 Hydrocarbons

The distribution of alkylated PAH in the East Timbalier study area was complex (Figure 9.9, Table D.29). In the sediments along the north-south transect, a maximum was observed at T3, 100 m south of the discharge; however, two other secondary peaks were also observed. One was associated with the discharge at T4 and the other near T8. Each maximum was separated by a site which had very low alkylated PAH content, suggesting very complex transport and

deposition patterns within the system. Although FFPI values were high (>0.8) at all the stations where alkylated PAH were high, minima (<0.2) were observed at the stations with low alkylated PAH. Aliphatic hydrocarbon concentrations (Figure 9.9) in the sediments along the north-south transect paralleled the patterns observed for alkylated PAH. Maxima were observed at the same three stations in approximately the same ratios. Very low concentrations were observed in the sediments where minima were observed.

Alkylated PAH contents of sediments along the east-west transect (Figure 9.10) were also variable with two maxima of approximately the same concentration. In general, where observed, these concentrations were lower than along the north-south transect (1,200 to 2,000 ppb vs. 5,000 to 19,000 for the maxima). A minimum was observed at the T12 site nearest the discharge with maxima observed both to the east and west of this site. Parent PAH were much more concentrated in the sediments along this transect than at most other locations in this entire study. FFPI values calculated for these sediment samples showed values >0.6 associated with the maxima and 0.3 or less for all of the other sites on this transect. Aliphatic hydrocarbon concentration profiles closely followed those of the alkylated PAH. Maxima and minima were observed at the same stations. As with the alkylated PAH, the total hydrocarbon contents of the sediments along the east-west transect were much lower than along the north-south transect.

The East Timbalier Island is a very complex study area. Our single set of samples revealed that produced water associated hydrocarbons were found in near-bottom waters and sediments. Because of the multiple discharges, as well as a discontinued discharge, the complex hydrology and sediment type distributions in the region, it was difficult to interpret the relationship of a particular discharge to the sediment residues found.

9.5.2 Trace Metals

Trace metal concentrations in surficial sediments from the East Timbalier study area are presented in Figure 9.11 and Table E.13. Barium concentration had a slight maximum along the north-south transect at station T4, which was located adjacent to a discharge. Barium concentrations in sediments at other stations were at similar levels adjacent to T4 and at stations to the north. It was not clear if these sediments were influenced by a specific discharge (current or discontinued) or there were higher barium levels at these stations because of the numerous oil treatment facilities in the area. Zinc followed a similar pattern as barium, with the exception of station T4 (Figure 9.11). Most of the other metals, which were not graphed, displayed similar distribution patterns; however, differences in concentration between stations were small. Metals and hydrocarbons displayed similar distribution patterns for both transects, indicating that the source of these analytes was the same.

9.5.3 Radionuclides

Surficial sediment Pb-210 activities in the East Timbalier Island study area showed no spatial trend (Figure 9.12, Table F.14) and ranged from 0.17 to 0.81 $\text{dpm}\cdot\text{g}^{-1}$. Surface sediment Pb-210 activities in coastal environments are typically about 2.0 $\text{dpm}\cdot\text{g}^{-1}$ (range: 0.1 to 5.0 $\text{dpm}\cdot\text{g}^{-1}$), depending on many factors controlling the sorption reactions (e.g., grain size, per cent organic carbon, turbidity in overlying waters). The values for East Timbalier Island are within the natural levels.

9.6 Benthic Biota

The benthic infaunal community of the East Timbalier Island study area was characterized by a marine fauna of mostly polychaetes and a few bivalves, gastropods, amphipods, isopods, cumaceans and nemerteans. There were large numbers of the opportunistic polychaetes *Streblospio benedicti*, *Mediomastus ambiseta* and *Capitella capitata*.

For convenience of presenting data in a geographically complex study design, the stations were divided into two transects, a north-south and an east-west, with overlap in station T9. Stations along the north-south transect were generally characterized by shallower water, sandier sediments, and a reduced current velocity because of the dead-end nature of the access canal. The stations along the north-south transect were also more typical of barrier island washover zones than the open Timbalier Bay environments of the east-west transect. Accordingly, the benthic fauna of the two transects differed in community parameters. In general, the stations along the north-south transect had fewer species and fewer individuals than those stations along the east-west transect (Figure 9.13, Table 9.2, Table G.21).

There were statistically significant differences among stations at the East Timbalier Island study area for all benthic community parameters (Table G.22). These differences were related to differences in the habitats of the north-south and east-west transects, as well as to proximity to a discharge point or level of chemical contaminants in the sediments. Station T3 differed statistically from all other East Timbalier Island stations in the low number of species and low number of individuals (Table 9.2). This station was near discharge point T-1 in a dead-end canal. Stations T5, T6, T7 and T8 had significantly fewer species than other stations in the north-south transect and the remainder of the study area (Table 9.2). Stations T4, T9 and T2 in the north-south transect were similar to each other, but differed in lower number of species from the stations in the east-west transect. There were statistically fewer individuals at stations T2 - T8 than at stations T1 and T9 in the north-south transect and those in the east-west transect.

Within the east-west transect, there were differences among stations with respect to most of the benthic community parameters. Station T13, opposite the discharge at Tank Battery #2, had significantly fewer number of individuals than the other east-west stations; the other stations did not differ from each other. While there were differences between stations in number of species, these differences were not along any obvious gradient in distance from a discharge point. The community parameters of diversity (H') and evenness (J') provided little information for discrimination of stations.

The benthic community parameters of number of species and number of individuals were related to some of the sedimentary characteristics and some sediment chemical constituents, but the relationships were not consistent between the stations in the north-south transect and those in the east-west transect. In general there were more species and more individuals at stations in the north-south transect with regards to increased sand content and reduced sediment organic content. For the east-west transect, there were more species and more individuals with reduced sand content and higher total organic carbon in the sediments. Where relationships were apparent with the benthic fauna and sediment hydrocarbon contamination, these relationships were stronger for stations in the north-south transect than the east-west. Examples of the relationships are shown in Figure 9.14 and threshold concentrations are given in Table 9.3.

9.7 Summary

The East Timbalier Island area was complex with regards to sedimentary characteristics, hydrological conditions and numerous produced water discharges (including one discontinued effluent at the time of the field studies). A total of 25,558 bbl·d⁻¹ produced waters were being discharged in the study area in February 1990. An additional 2,429 bbl·d⁻¹ was present pre-1988. The discharges and sample stations were located within a complex of dredged access canals and natural water bodies. The access dead-end canal which was situated north-south in the study area was shallower, had sandier sediments typical of a back barrier washover area, and more sluggish tidal currents. The remaining stations were located along an east-west transect parallel to the back side of the island along the southern end of Timbalier Bay. The east-west stations had siltier sediments, were deeper, and were exposed to a more energetic tidal regime.

The single monitoring of currents indicated that high bed shear stress capable of resuspending and transporting sediments did occur but was of short duration. Variations in the current regime indicated a net movement of water on the flood, or south into the access canal system. No indication of a bottom-hugging density plume from a produced water was evident from the CTD data except at station T3, 100 m to the southwest of a discharge.

Near-bottom water samples indicated petrogenic hydrocarbon contaminants near a discharge (station T4 near T-1) or within 250 m of that discharge point. Pb-210 activities in the near-bottom waters were all within natural levels except at station T7 in the north-south canal. On the other hand, total radium activities in near-bottom waters were elevated throughout the study area at 15 to 45 times the expected natural levels.

Levels of sediment contaminants, including hydrocarbons and trace metals, were higher along the north-south transect than the east-west one. Within the north-south transect, elevated petrogenic hydrocarbons were evident at station T4 near the discharge point and at stations T3 and T8, which were in dead-end channels. If similar hydrologic conditions exist through parts of the year as during the 26-hr monitoring of currents, then transport of sediment-adsorbed contaminants could be expected and stations T3 and T8 might be depositional areas for these transported sediments. Along the east-west transect, elevated levels of petrogenic hydrocarbons were apparent at stations T14 and T10 which were not adjacent to the discharge points but near them. Stations adjacent to the discharge points did not exhibit elevated levels of the same contaminants. Pb-210 activities for East Timbalier Island study area sediments were within expected natural levels.

The benthic fauna of the area differed, as did the hydrocarbons and trace metals, between the two transects. There were generally fewer species and fewer individuals along the north-south transect than the east-west transect. Station T3 had significantly fewer species and individuals than other stations in the whole study area, as well as the highest levels of petrogenic contaminants. Other differences in species and numbers in the study area were identified, but there was considerable overlap in the means for the stations. Still, where there were reductions in fauna, there were also elevated levels of some chemical constituents in the sediments.

A preliminary survey of the benthic communities was made in January 1988 for the Boesch and Rabalais (1989a) study. Severely depressed benthic communities (in both number of species and number of individuals) were found at two locations in the north-south canal at approximately stations T5 and T9 of this study. Unfortunately, the chemistry sample for the T9 equivalent was lost due to breakage, but total PAH was elevated in the stations of the T5 "equivalent" (2,300 ppb). Total saturated HC were also high (57,000 ppb), and the FFPI value (0.87) indicated a petrogenic origin. These threshold levels (in Boesch and Rabalais 1989a) were lower than those found in this study (see Table 9.3). Overlying water volatiles and total PAH at a single station in the Boesch and Rabalais (1989a) study exceeded those found in this study. Otherwise, sediment contaminants in the previous study were within those reported here.

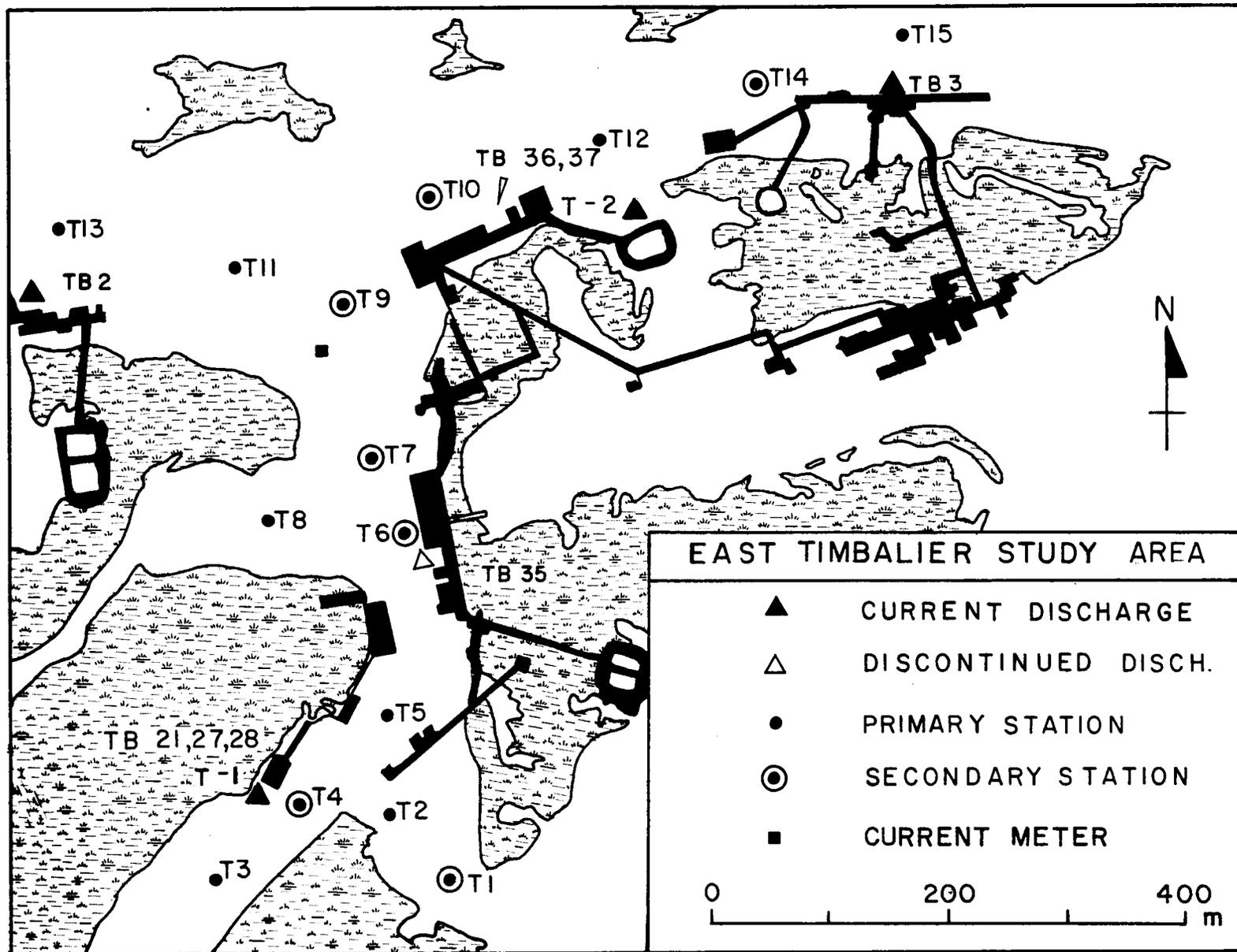


Figure 9.1. East Timbalier Island study area.

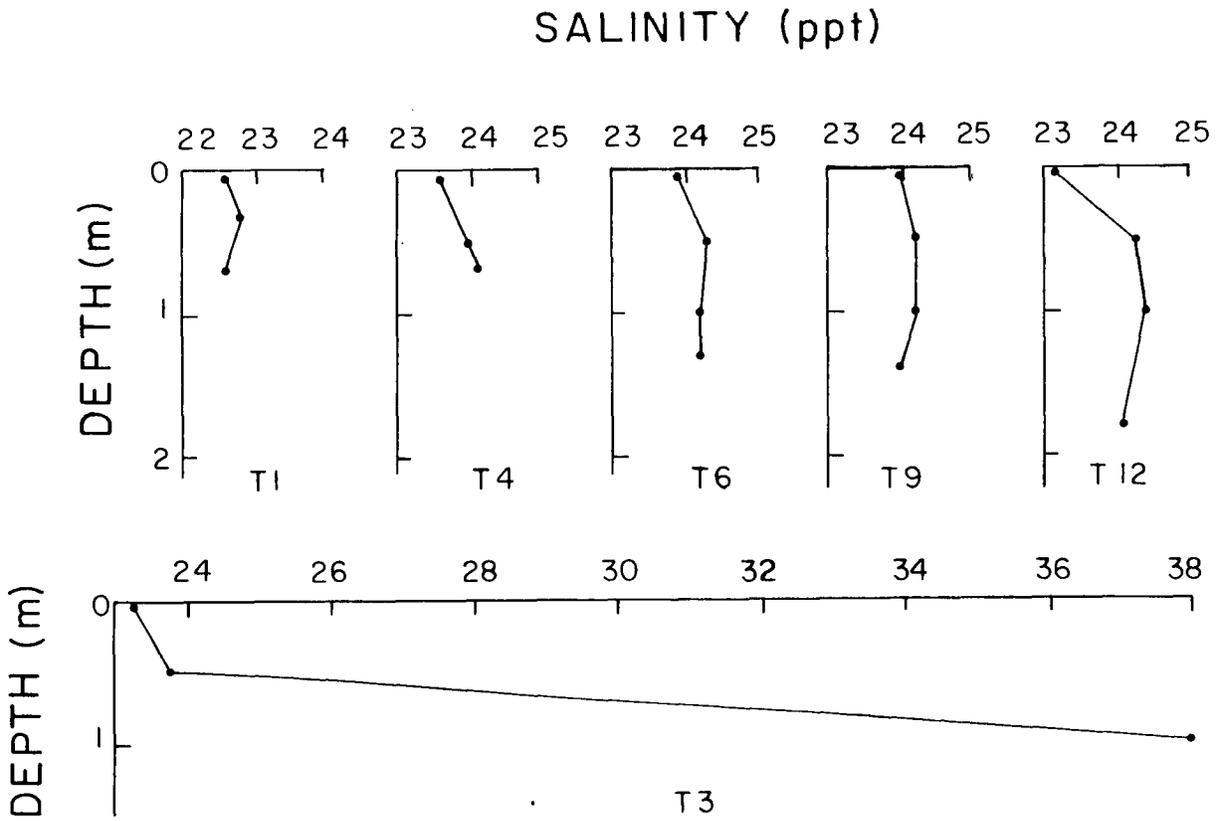


Figure 9.2. Salinity distribution through the water column at selected stations for East Timbalier Island, May 1989.

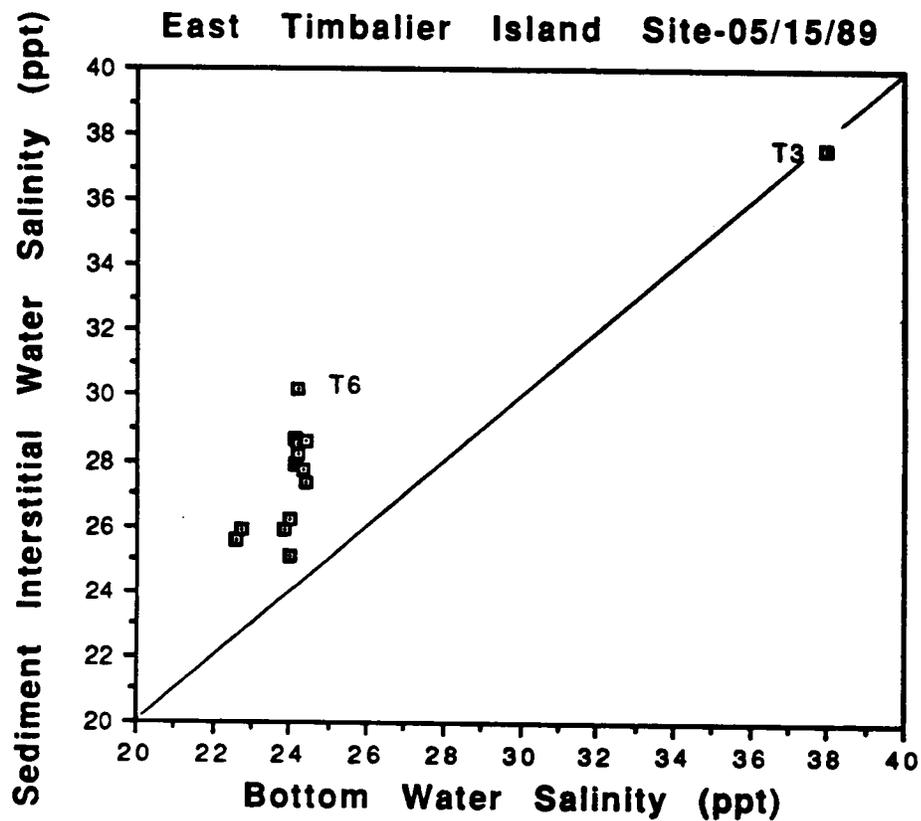


Figure 9.3. Comparisons of interstitial water salinity from surface sediments of stations in the East Timbalier Island study area and near-bottom water salinity. Station number given for value most different from a 1:1 relationship (indicated by diagonal line) and for station affected by density plume.

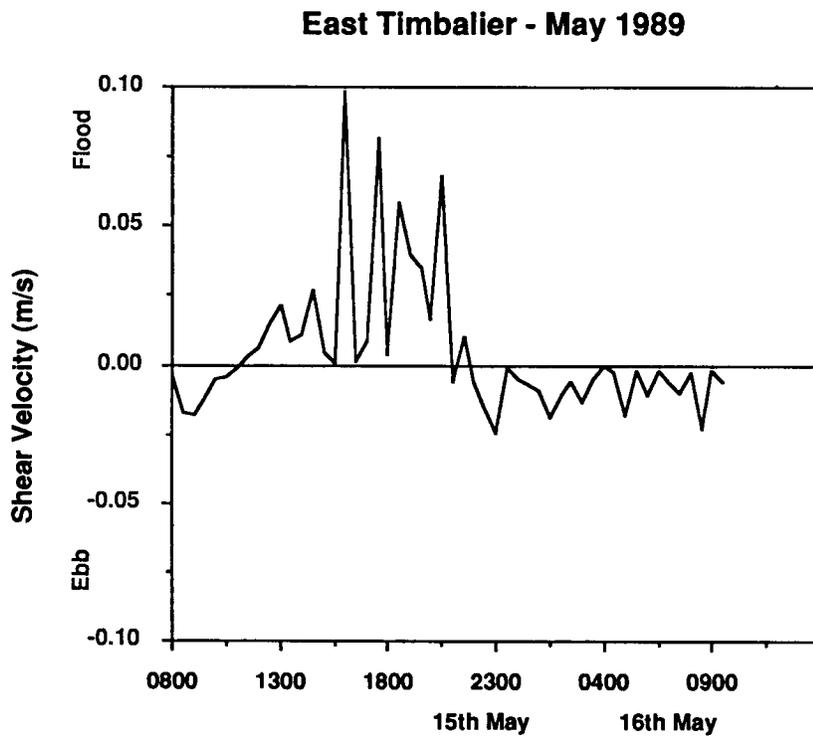
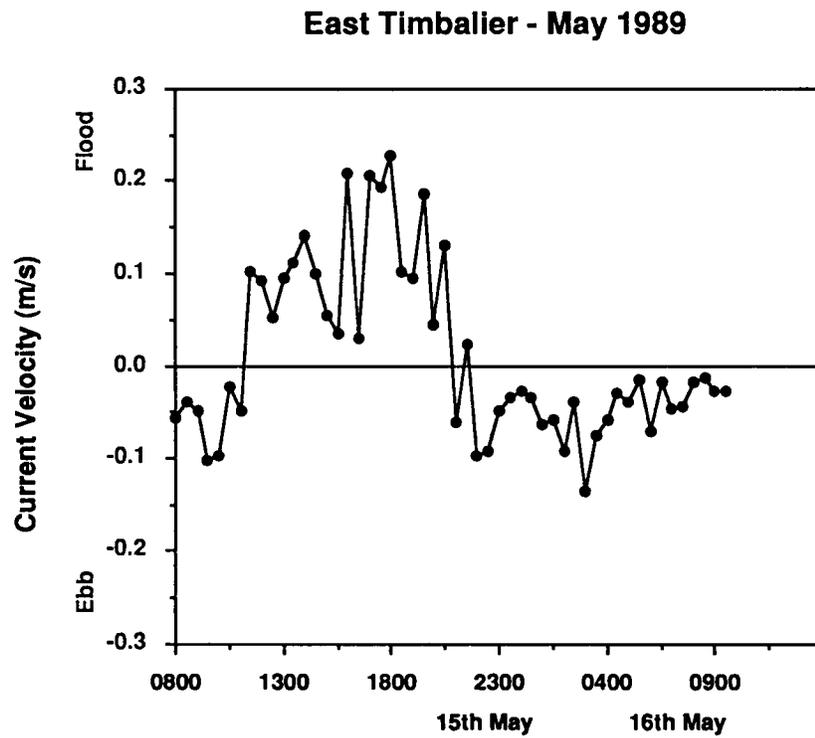


Figure 9.4. Mean tidal current velocity variation and calculated shear velocities for East Timbalier Island, May 1989.

EAST TIMBALIER: MAY 1989

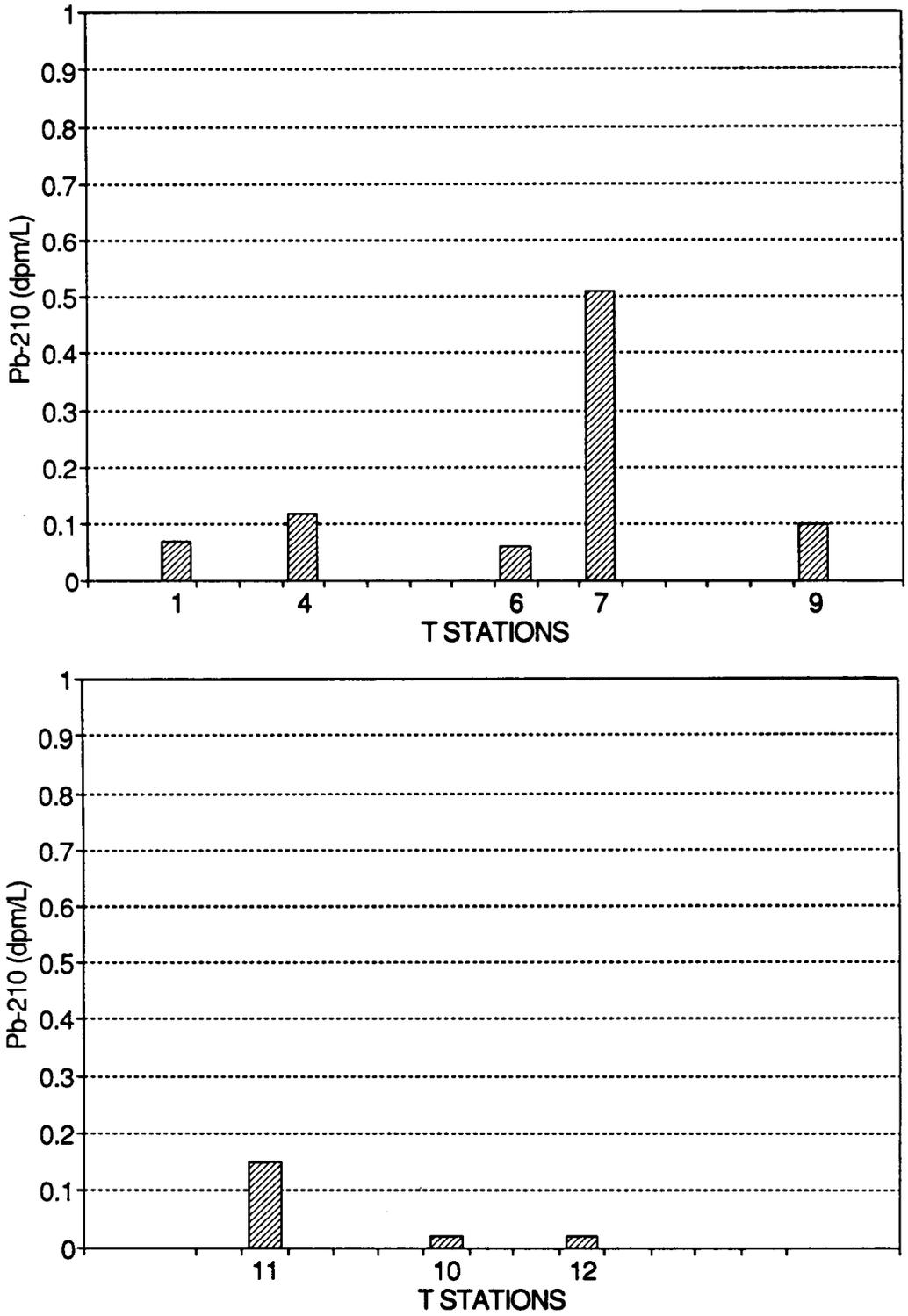


Figure 9.5. Spatial distribution of Pb-210 activities in East Timbalier Island near-bottom waters, May 1989.

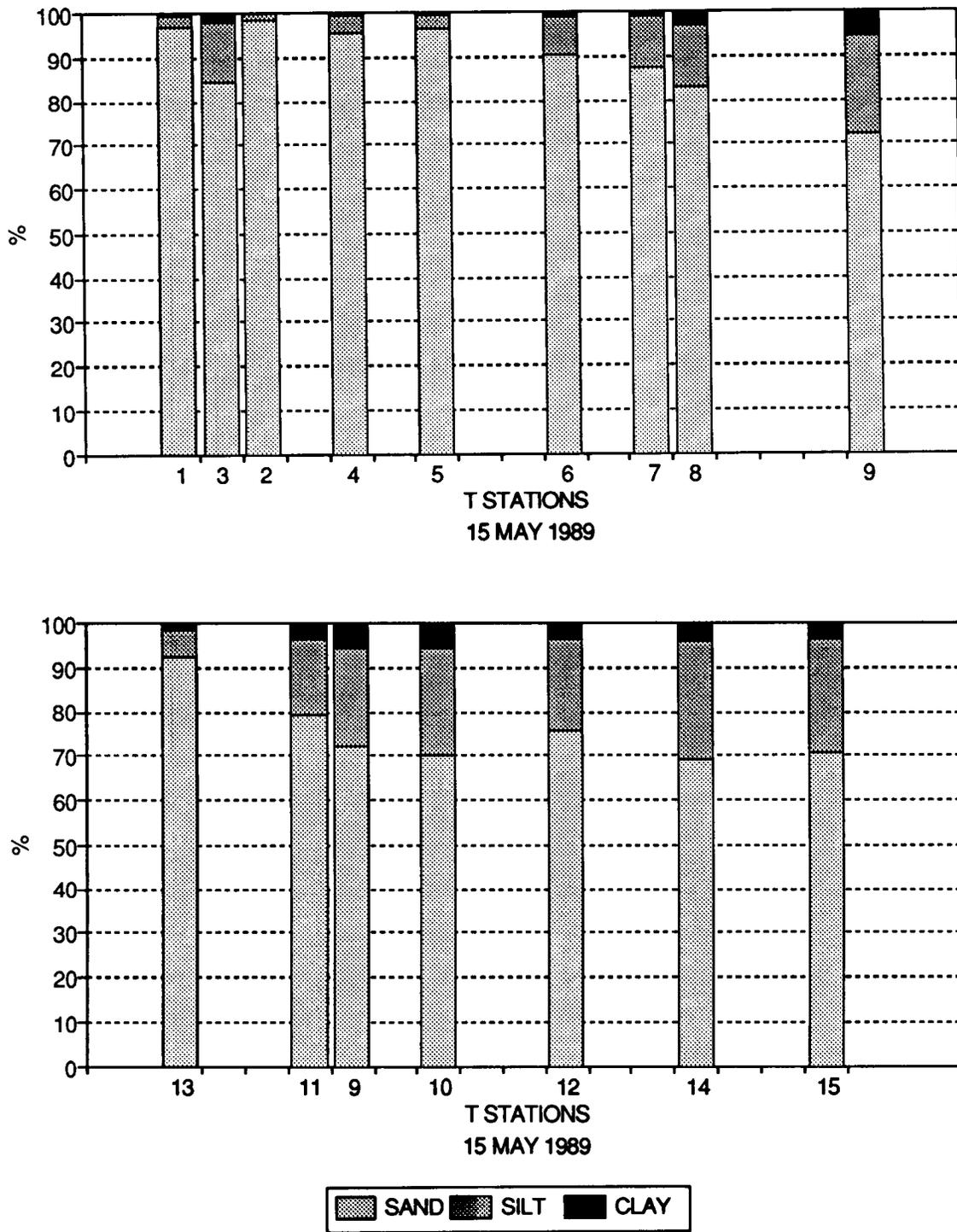


Figure 9.6. Spatial distribution of surface sediment grain size from East Timbalier Island, May 1989.

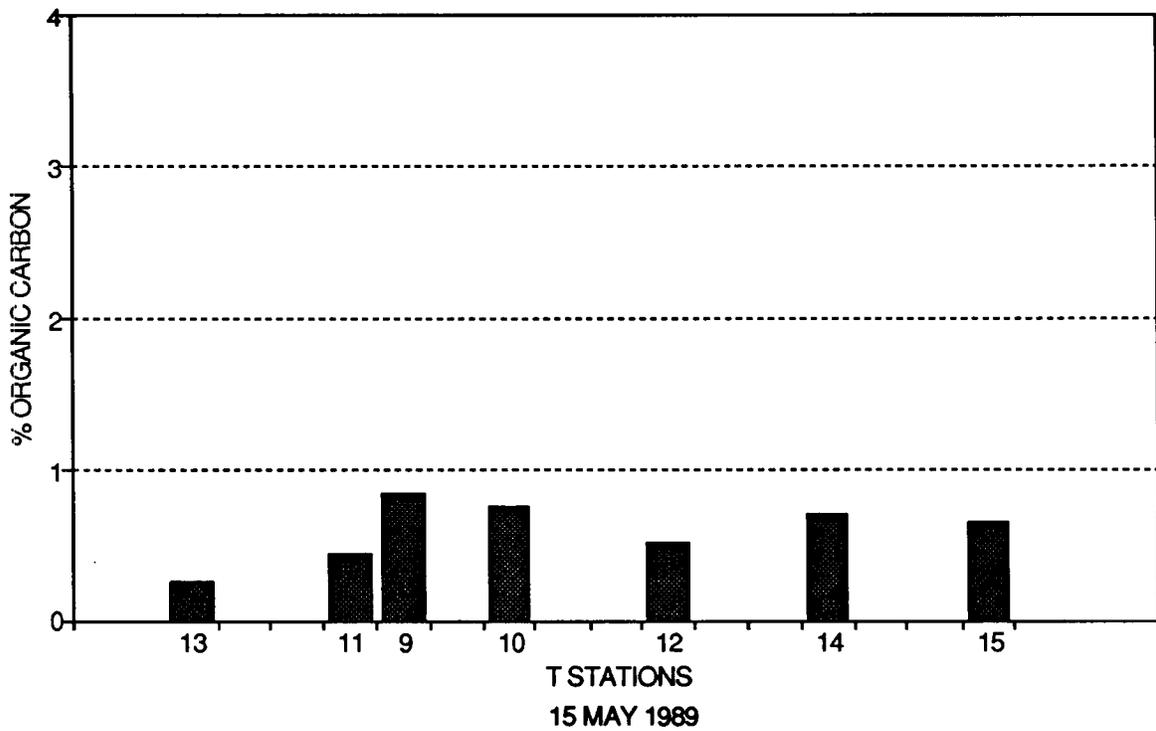
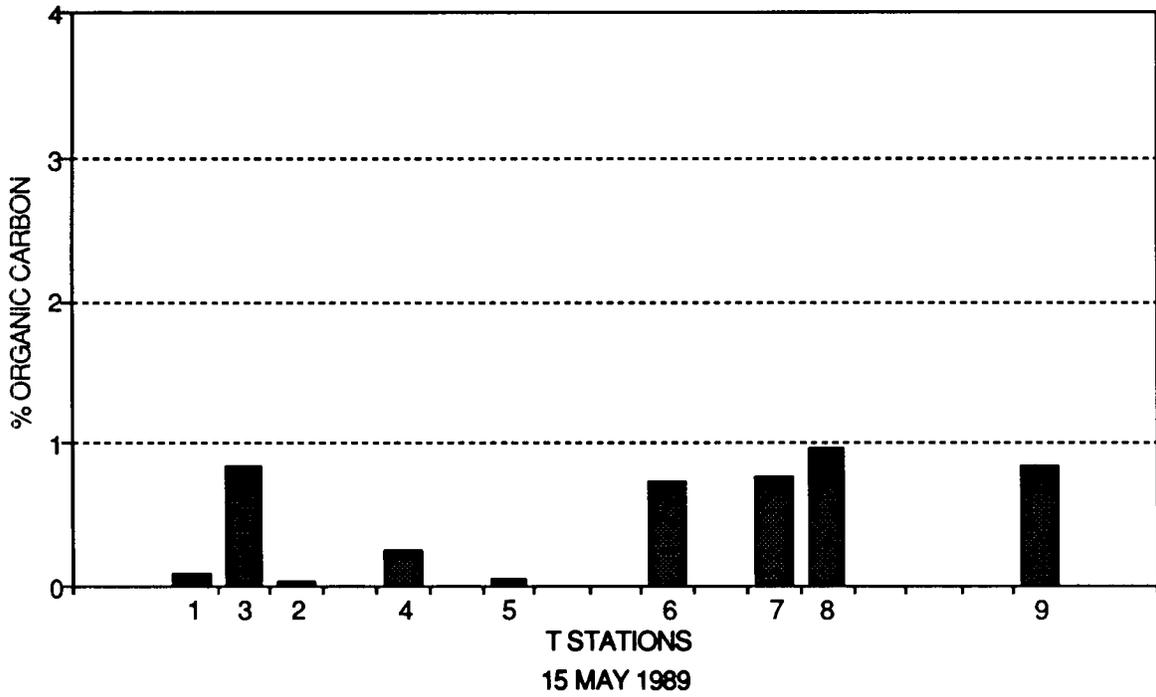


Figure 9.7. Spatial distribution of percent total organic carbon in surface sediments from East Timbalier Island, May 1989.

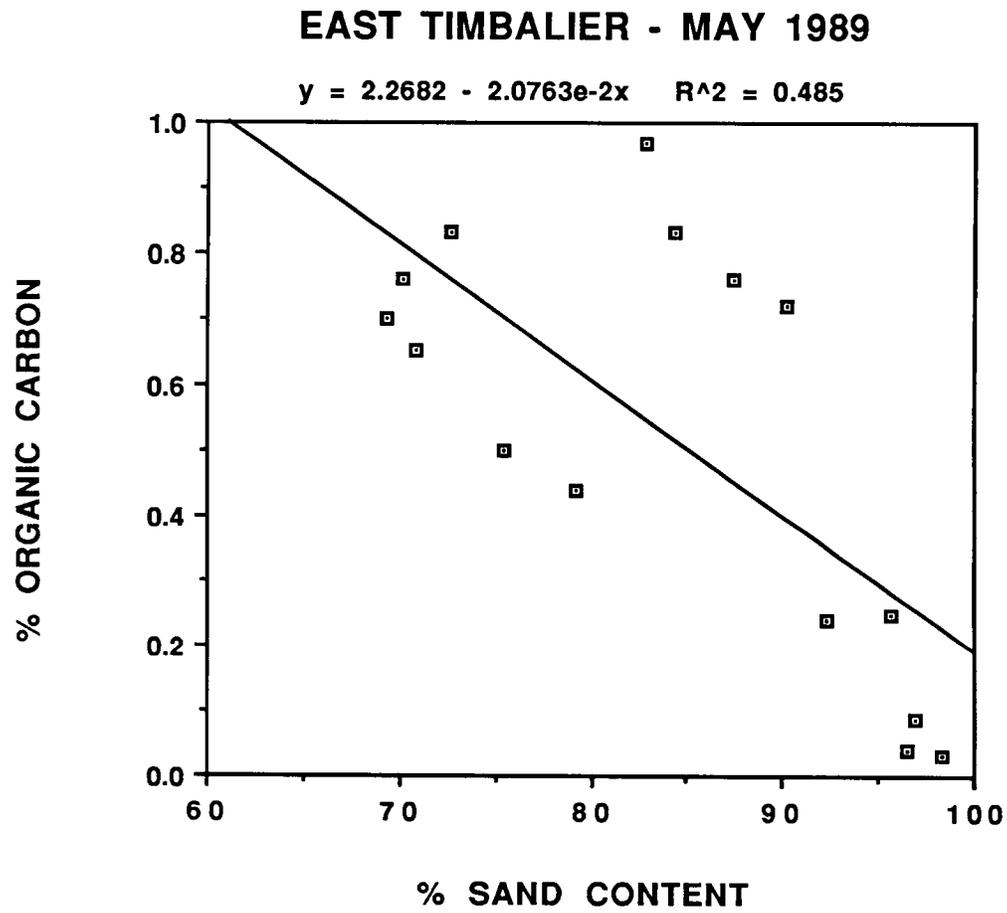


Figure 9.8. Comparison of percent total organic carbon and percent sand content of surficial sediments from East Timbalier Island, May 1989.

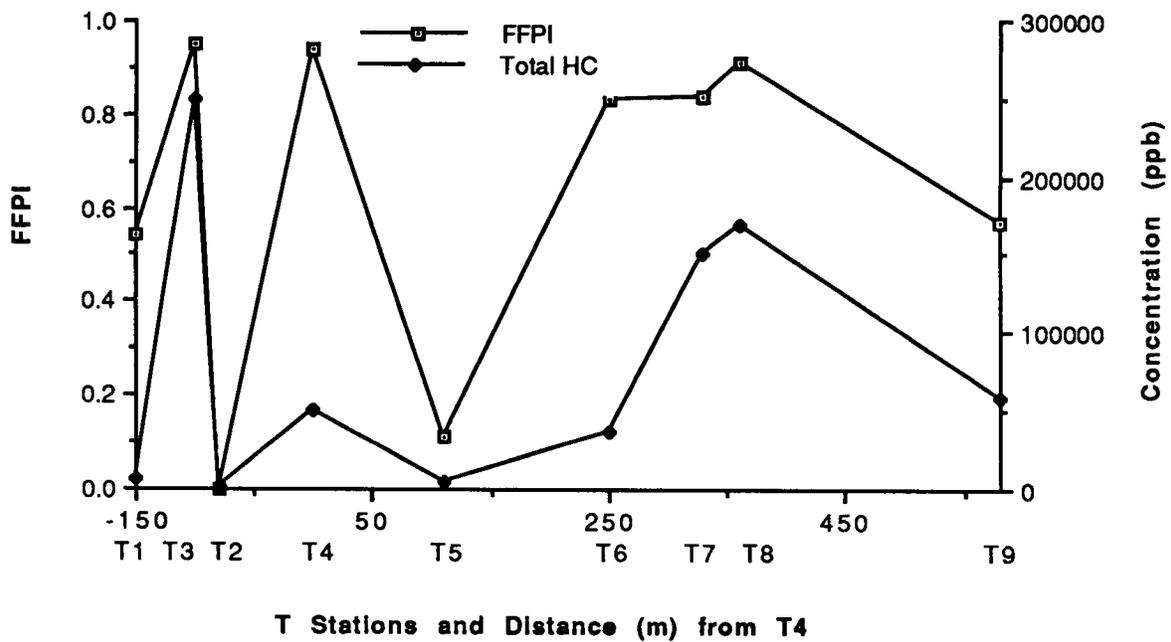
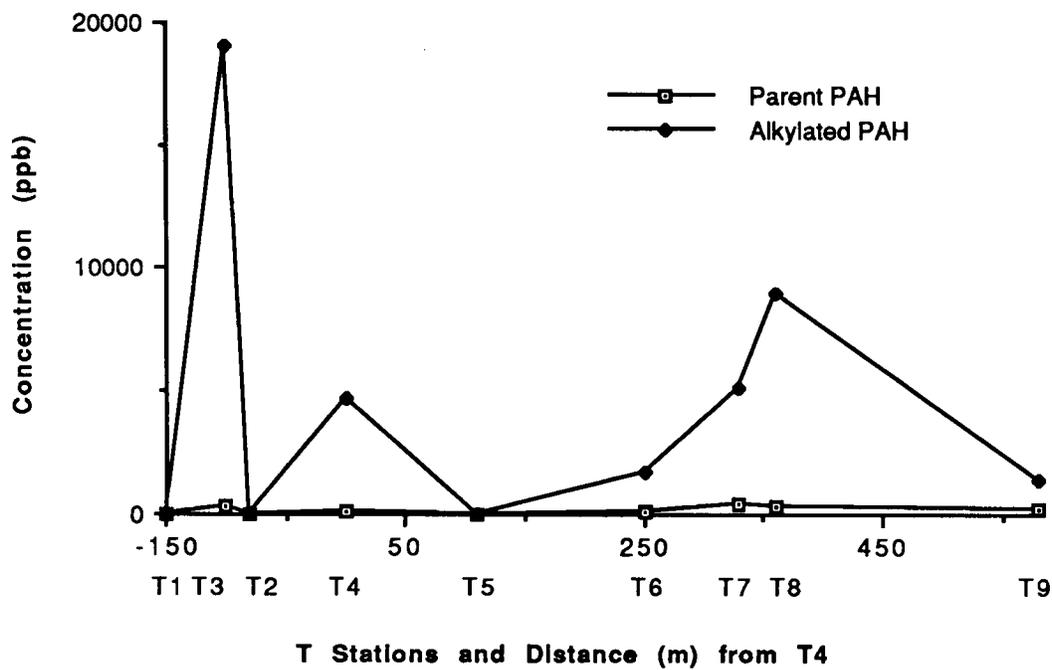


Figure 9.9. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from the north-south transect at East Timbalier Island, May 1989.

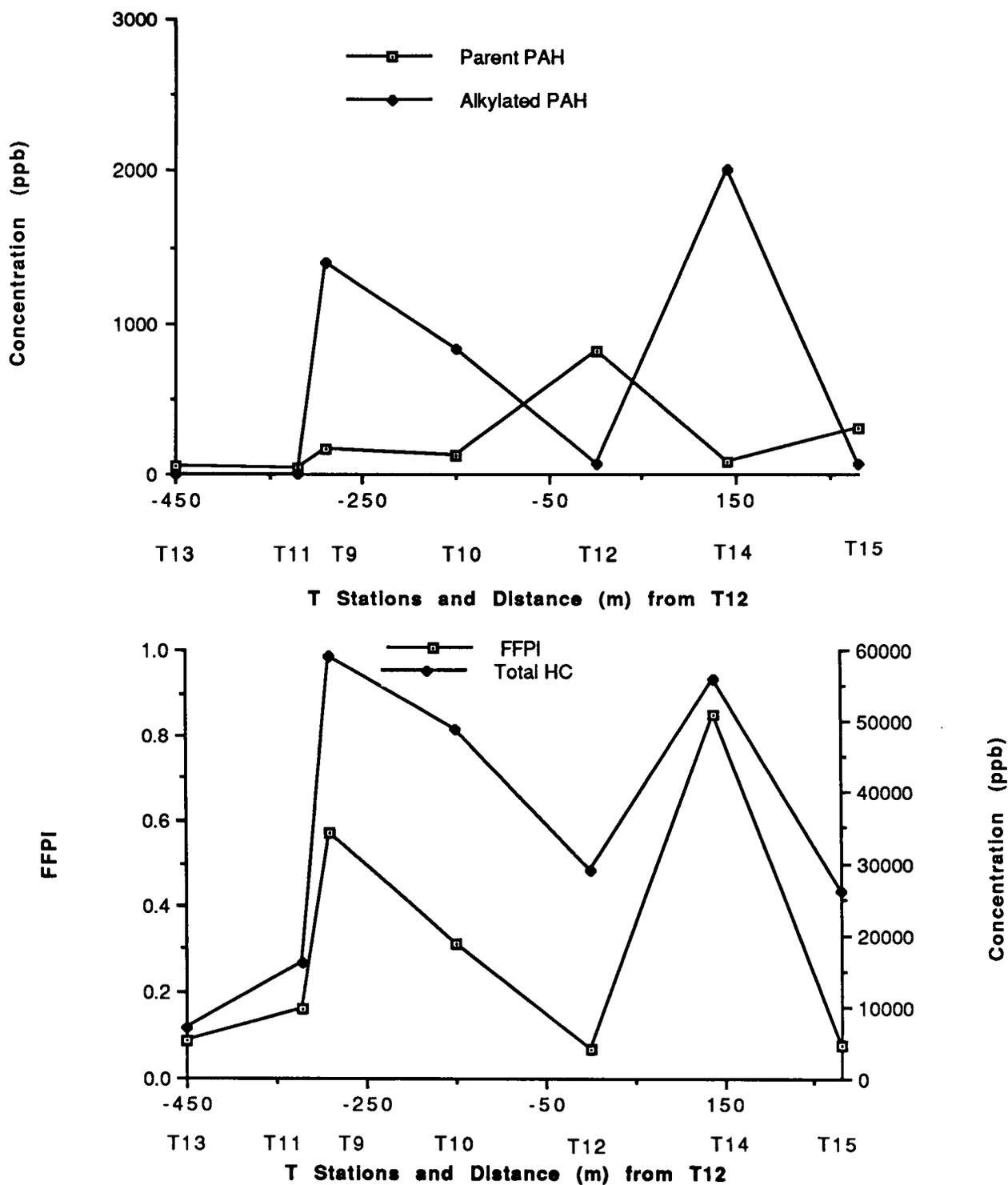


Figure 9.10. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from the east-west transect at East Timbalier Island, May 1989.

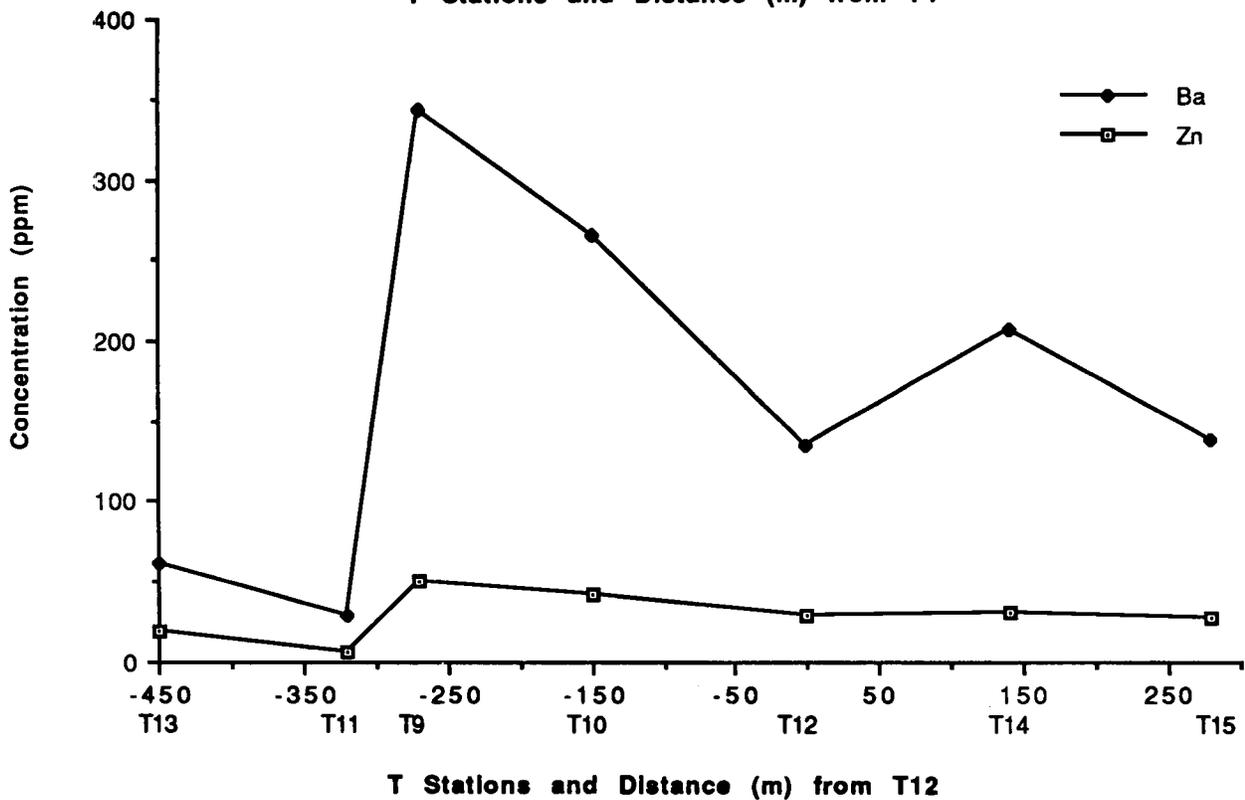
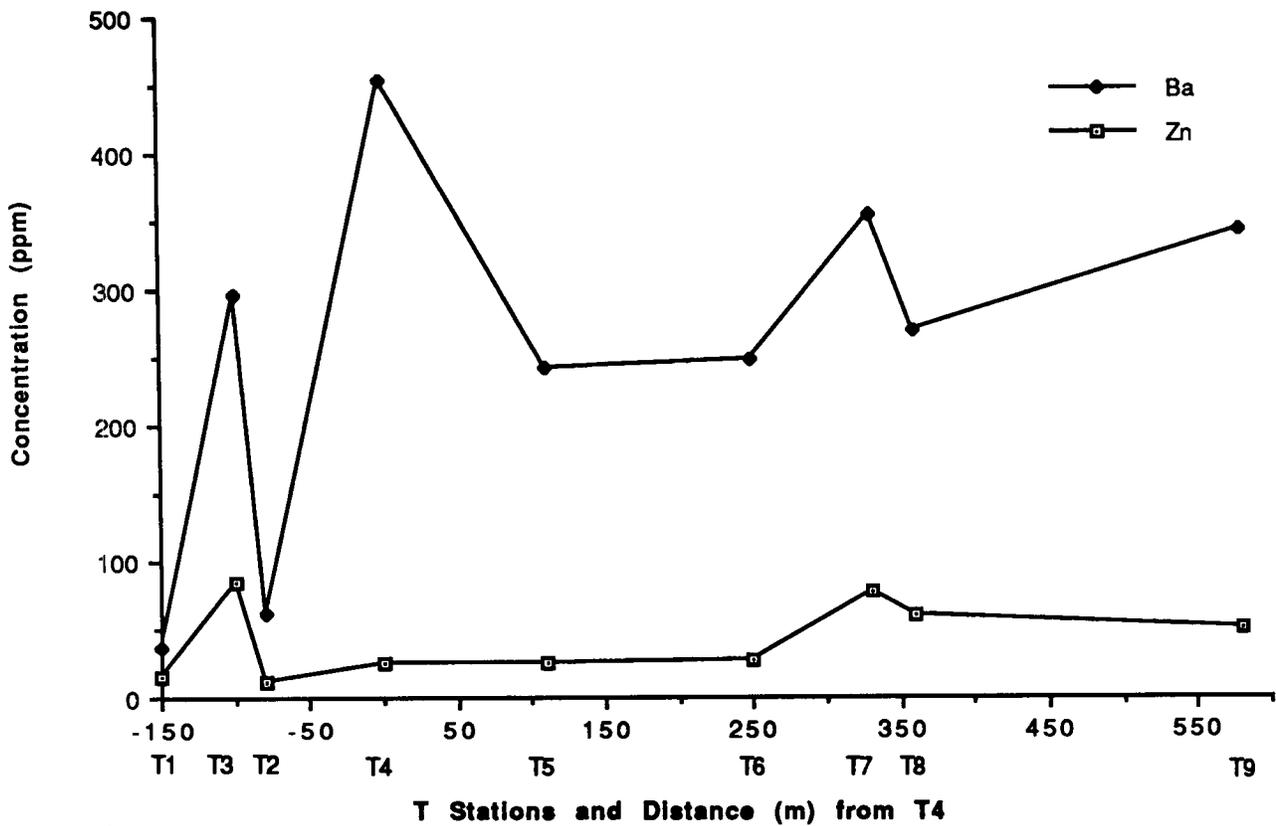


Figure 9.11. Spatial distribution of selected trace metal concentrations in surface sediments from East Timbalier Island, May 1989.

EAST TIMBALIER: MAY 1989 SURFACE SEDIMENT Pb-210

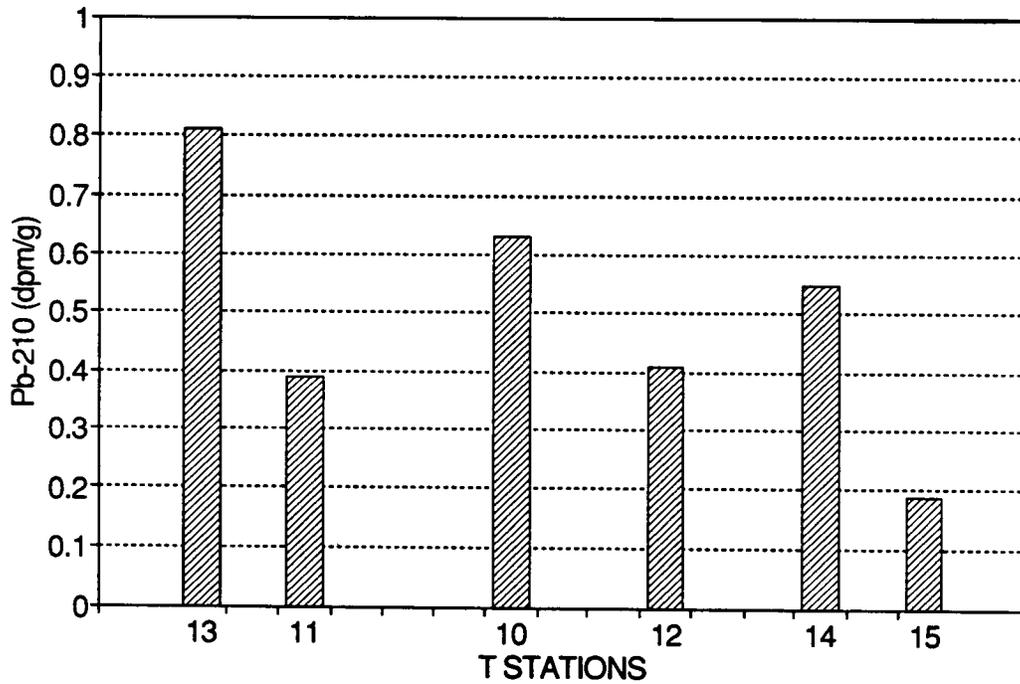
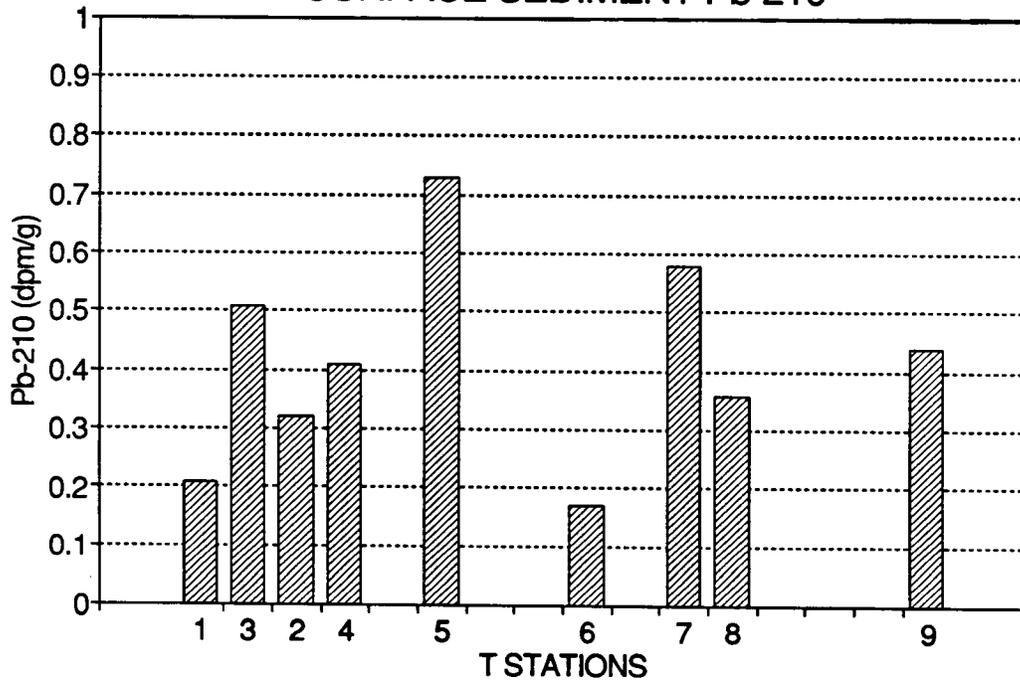


Figure 9.12. Spatial distribution of Pb-210 activities in surface sediments from East Timbalier Island, May 1989.

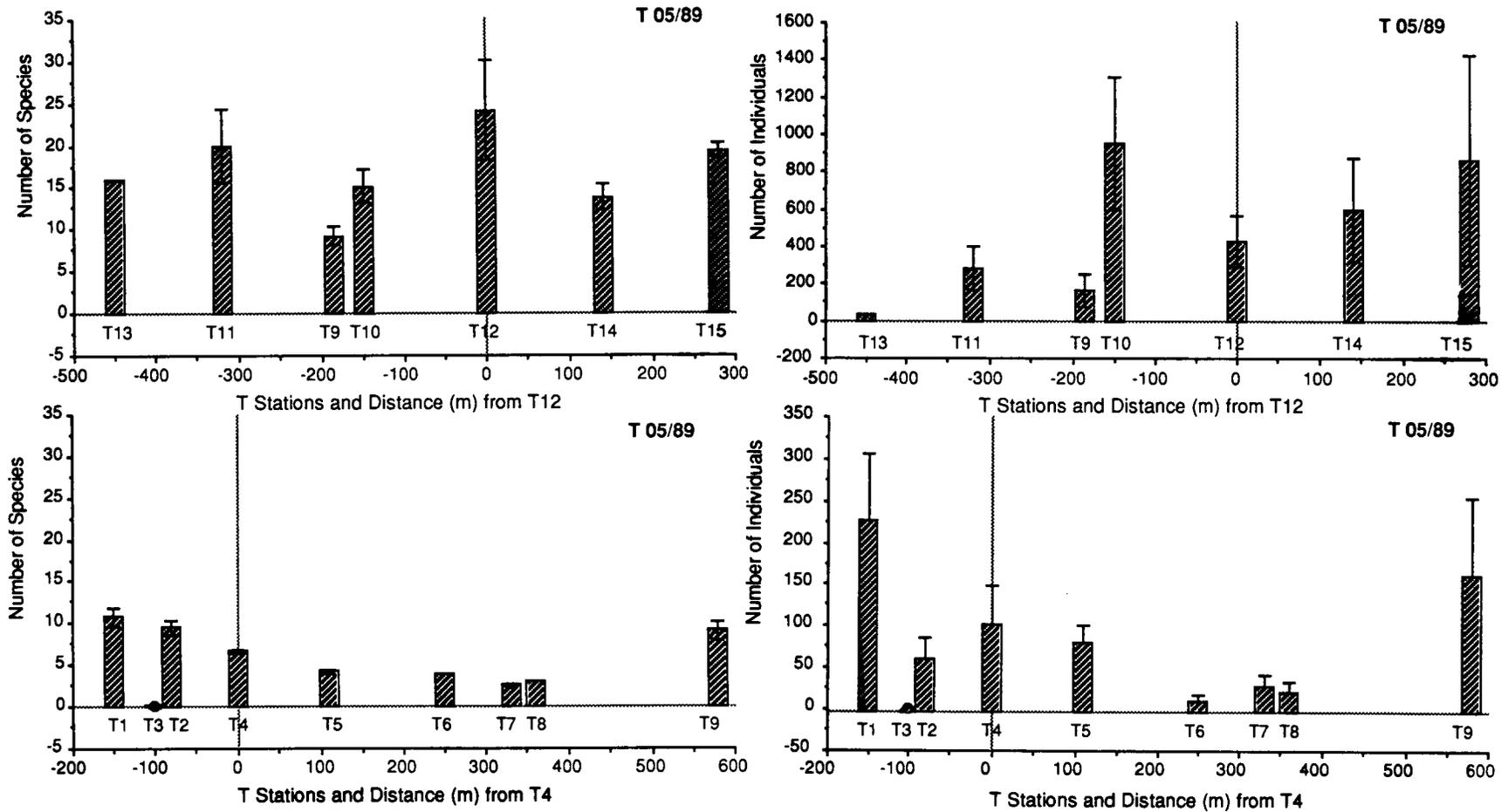


Figure 9.13. Spatial distribution of number of species per replicate (mean \pm standard error) and number of individuals per replicate (mean \pm standard error) for East Timbalier Island, May 1989.

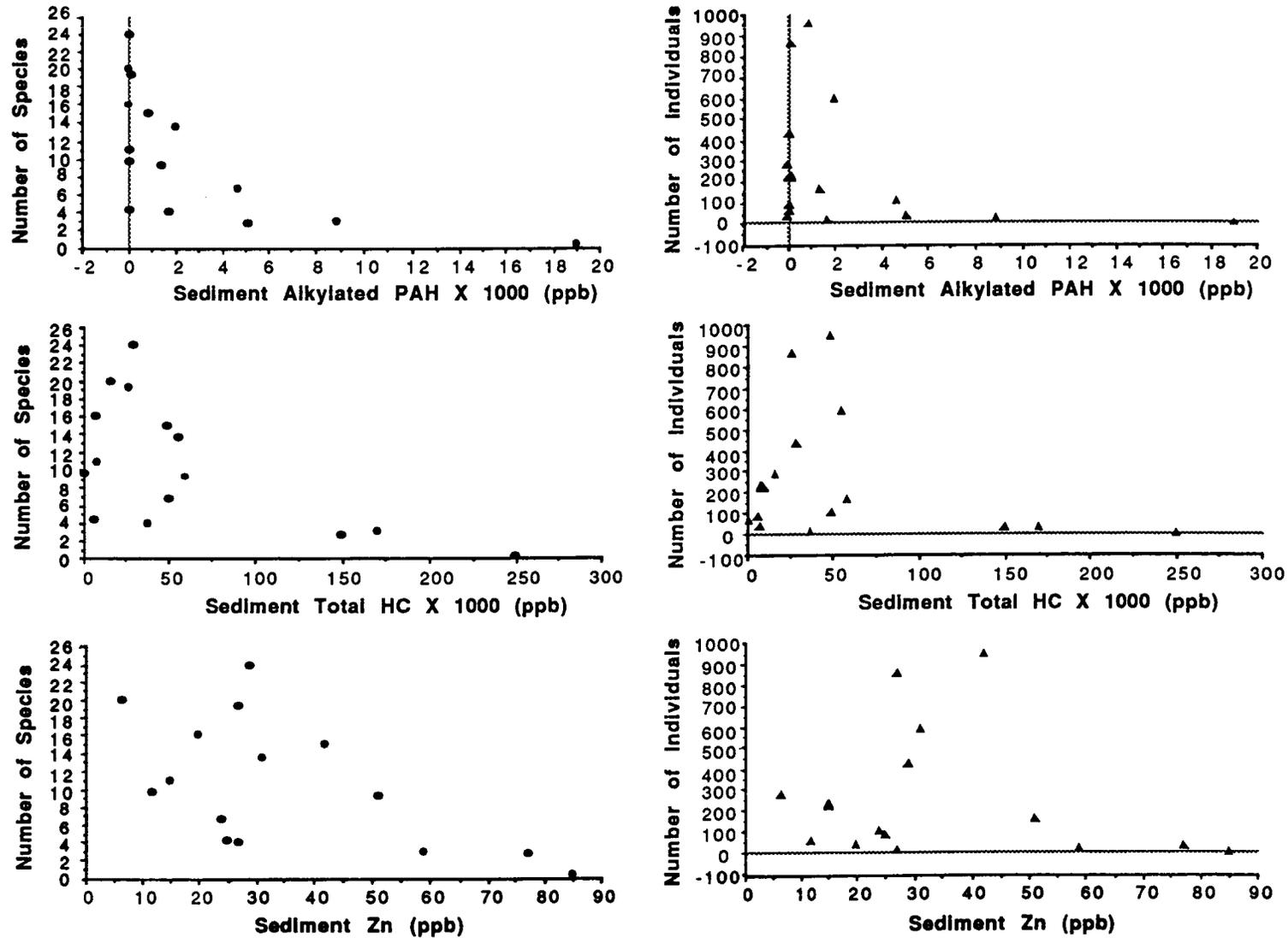


Figure 9.14. Relationships of mean number of species per replicate and mean number of individuals per replicate to various sediment contaminants for East Timbalier Island.

Table 9.1. Comparison of average daily discharges (bbl·d⁻¹) and oil and grease content (mg·l⁻¹) of produced waters from facilities at the East Timbalier Island study area. Volumes in <brackets> are discontinued (as of 03/91). (Data provided by operators; N/A = not available.)

Date	Facility				
	T-1 TB 21, 27, 28 (was OCS)	T-2 TB 36, 37 (OCS)	TB 35 (was OCS)	TB 2 (State)	TB 3 (State)
05/89					
Discharge	15,592	5,200	----	6,520	2,301
Oil and Grease	15	9	----	15	9
Average Discharge	<13,258>* 24*	5,005* 20*	<5,672>** 17**	4,866* 19*	2,429* 21*
Average Oil and Grease					
Discharge Estimated in Boesch and Rabalais (1989a)	20,000	2,862	1,196	N/A	8,000
Discharge as of 03/91	0	8,500	0	N/A	N/A

* Mean of 25 monthly sample dates from 02/88 - 02/90.

** Mean of 7 monthly sample dates prior to discontinuation of discharge.

Table 9.2. Duncan's multiple range test for East Timbalier Island study area; underlined stations are not significantly different from each other.

Number of Species (natural log transformed):

3	7	8	6	5	4	9	2	1	14	10	13	11	15	12
_____										_____		_____		
_____				_____				_____				_____		

Number of Individuals (natural log transformed):

3	6	8	7	13	2	4	5	9	1	11	12	14	15	10
_____										_____		_____		
_____				_____				_____				_____		

* Diversity (H'):

3	7	14	5	10	8	4	9	6	1	15	12	2	11	13
_____										_____		_____		
_____				_____				_____				_____		

** Evenness (J'):

14	10	15	7	5	9	12	1	4	11	2	6	8	13	
_____										_____		_____		
_____				_____				_____				_____		

* Cell sizes unequal due to missing values.

** Cell sizes unequal due to missing values. Station T3 excluded from analysis due to zero values for all replicates.

Table 9.3. Concentrations of various chemical constituents in surficial sediments at East Timbalier Island at or above which there was a depressed benthic fauna.

Chemical Constituent	Number of Species	Number of Individuals
Surficial Sediments:		
Alkylated PAH ($\mu\text{g}\cdot\text{g}^{-1}$)	5,000	5,000
Total PAH ($\mu\text{g}\cdot\text{g}^{-1}$)	5,700	4,700
Total Saturated HC ($\mu\text{g}\cdot\text{g}^{-1}$)	150,000	150,000
Zn ($\mu\text{g}\cdot\text{g}^{-1}$)	58	58

Chapter 10

ROMERE PASS STUDY AREA

10.1 Description of Study Area

10.1.1 Facilities

There are two discharges of produced waters at the Romere Pass study area. One is generated on the Federally-controlled OCS (RP-1 OCS) and the second is generated within the State's territorial sea (RP-2 State) (Figure 10.1). Both discharges empty into Romere Pass. Romere Pass, on its southern end, joins Main Pass which is a major distributary of the Mississippi River delta. During flood stage of the river, much of the marsh is inundated. During low flow of the river, freshwater inflow from the river affects the southern end of Romere Pass. The northern end of Romere Pass joins East Fork which enters Breton Sound where higher salinities are found. Thus, north-south differences in salinity existed in October 1989 during low flow within the 2-km long study area. Vegetation in the area was typical freshwater marsh flora. The Romere Pass study area is located within the Delta National Wildlife Refuge. Although there are oil and gas facilities within the area, there are none within 2 km of the Romere Pass treatment facility.

The combined discharge of produced waters from the two facilities at the Romere Pass study site was approximately $20,000 \text{ bbl}\cdot\text{d}^{-1}$ in February 1990. The discharges are identified as follows:

RP-1 OCS is the Chevron U.S.A. Inc. Main Pass Block 41 Terminal operation. The facility is owned by Chevron Pipe Line Company but operated by Chevron U.S.A. Inc. The facility was installed in 1965 and has been in continuous operation since. The average daily discharge rate was $3,021 \text{ bbl}\cdot\text{d}^{-1}$ over a 25-month period from February 1988 - February 1990 (Table 10.1) and was $1,392 \text{ bbl}\cdot\text{d}^{-1}$ at the time of the field studies. Over the same 25-month period, the discharge rate has been stable. The hydrocarbon levels, reported as oil and grease, averaged $16 \text{ mg}\cdot\text{l}^{-1}$; the chloride levels were reported at 67,210 ppm (121 ppt salinity). A series of clarifiers, demulsifiers and bacteriocides are used at the facility; no unusual activities were known to have taken place near the time of sampling. The point of discharge is a pipe which extends directly onto the surface waters of Romere Pass (Figure 10.1).

Chevron U.S.A. Inc. also operates the Romere Pass facility (RP-2 State) which treats produced water generated within the State's jurisdiction. The facility was installed in 1952 and has been in continuous operation since. The average discharge rate was $17,137 \text{ bbl}\cdot\text{d}^{-1}$ over a 25-month period from February 1988 - February 1990 (Table 10.1) and was $14,408 \text{ bbl}\cdot\text{d}^{-1}$ at the time of the field studies. Over the same 25-month period, the discharge rate has been stable. The hydrocarbon levels averaged $16 \text{ mg}\cdot\text{l}^{-1}$; the chloride levels were reported at 27,370 ppm (49 ppt salinity). Clarifiers and bacteriocides are used in the treatment process; no unusual activities were known to have taken place near the time of sampling. The produced waters are retained in a settling pond with a pipe that releases water through gravity flow into a discharge pipe under the facility alongside Romere Pass near station RP550N (Figure 10.1).

10.1.2 Study Design

A series of stations were located along the length of Romere Pass where it was navigable by the research vessel *Acadiana* and where the *Acadiana* could maneuver and anchor in the high winds that existed on the day of sampling (Figure 10.1). Romere Pass was a difficult area to sample from the R/V *Acadiana* during the extreme low tide and low river flow conditions. The

pass was shallow and the channel, narrow. Combined with strong north winds (25 to 40 knots), the local physiography dictated some station locations. Station locations suggested for a uniform coverage of the pass had to be modified so that stations could be situated where the vessel could be anchored. A station was situated in the pass adjacent to each discharge (RP0 at discharge RP-1 OCS, and RP550N at discharge RP-2 State). There were eight stations total, of which four were "secondary" stations from which near-bottom waters and vertical sediment cores were collected. Adequate surficial sediment samples were collected, but deep vertical sediment cores were not at most stations because of compacted, fine sandy sediments. On the northern end of Romere Pass, the sediments were siltier and deeper cores were possible. Current meter measurements were taken from onboard the *Acadiana* at a fixed position halfway between RP550N and RP250N for part of the study period and at various locations during benthic sampling for the remainder. Sampling was conducted in October 1989.

The data for the Romere Pass study site are plotted as a function of the distance away from the point of the OCS produced water discharge. Station numbers reflect the distance in meters away from this discharge and the direction.

10.2 Hydrography

10.2.1 Hydrographic Profiles

Salinity profiles for Romere Pass stations indicated a well-mixed water column with differences in salinity on a north-south gradient (Figure 10.2, Table A.14). Stations on the northern end were higher in salinity (approx. 8 ppt). Salinities in the middle section of the study area were between 5 and 7.5 ppt. The most southerly station (RP750S) showed the influence of Main Pass, a major distributary of the Mississippi River. There was a slight increase in the bottom water salinity at station RP550N (1 ppt difference from the surface water). Water temperatures were near 16°C for all stations and all depths. The water column was well-oxygenated at all stations. Elevated levels of sulfides were measured at three of the four stations where near-bottom waters were collected and were trace at the fourth (Table A.14, Figure 10.2).

10.2.2 Dispersion of Effluent

The salinities for the produced water discharges at Romere Pass were 43 ppt (RP-1 OCS) and 98 ppt (RP-2 State). An effluent density plume for the produced water discharge was not evident from the water column CTD casts. The interstitial salinity of surficial sediments collected from box cores were not unusually elevated above the ambient levels (Figure 10.3). The sulfide concentrations of the discharges were moderate ($3.6 \mu\text{g-at S}\cdot\text{l}^{-1}$ for RP-2) to high ($48 \mu\text{g-at S}\cdot\text{l}^{-1}$ for RP-1) (Table C.1). The presence of sulfides in the near-bottom waters in the Romere Pass study area may be an indicator for the produced water discharge effluent.

10.2.3 Tidal Current Regime

Severe weather conditions, including gale force winds, prevented the use of a small boat for current monitoring at Romere Pass in October 1989. Current meter measurements were taken from R/V *Acadiana*. They were obtained from a fixed station between RP250N and RP550N between 1830 on 18 October and 0530 on 19 October, and between 1700 and 1730 on 19 October. Additional measurements were taken at the various sampling stations between 0900 and 1430 on 19 October. Both flood and ebb flows were identified (Figure 10.4). Velocities were very low towards the end of the ebb and at the beginning of the flood, less than $0.1 \text{ m}\cdot\text{s}^{-1}$. The predicted tide at Head of Passes on the Mississippi River was 1.4 ft for 18 October. The steady 20 knot ($10.3 \text{ m}\cdot\text{s}^{-1}$) wind from the north, increasing to 25 knots ($12.9 \text{ m}\cdot\text{s}^{-1}$) by 0900, probably retarded the ebb flow out of Romere Pass to the north. The northerly winds may also have accounted for the increased flood velocities, up to $0.52 \text{ m}\cdot\text{s}^{-1}$,

monitored between 0900 and 1430 on 19 October. The incomplete set of readings obtained from Romere Pass, and the severe wind conditions, made interpretation of the tidal current regime difficult. In summary, Romere Pass, a minor distributary of the Mississippi River, was tidal during monitoring October 1989, and stronger currents were recorded on the flood than on the ebb.

10.2.4 Velocity Profiles

Although the velocity profile data for Romere Pass was incomplete, shear velocities have been calculated where possible (Figure 10.4). During the late ebb and early flood shear velocities were low, generally less than $0.01 \text{ m}\cdot\text{s}^{-1}$, and sediment entrainment at the bed was unlikely. However, during the mid-flood tide when mean velocities increased, shear velocities were also higher, generally greater than $0.02 \text{ m}\cdot\text{s}^{-1}$ and reaching $0.07 \text{ m}\cdot\text{s}^{-1}$. Under these conditions sediment may be entrained and transported in Romere Pass. The beginning of the ebb, recorded late on 19 October, showed higher shear velocities which may also entrain bed sediments. The incomplete nature of the readings for Romere Pass made it difficult to infer either a net flood- or ebb-directed movement of sediment.

10.3 Water Column Contaminants

10.3.1 Hydrocarbons

Three out of four water samples of near-bottom waters in Romere Pass contained detectable levels of volatiles and PAH (Figure 10.5, Table D.14). Near-bottom water from station RP500N, adjacent to the RP-2 State discharge, contained the highest levels of hydrocarbons, with the more water soluble naphthalenes the only PAH detected in all three samples. Station RP0 was opposite discharge source RP-1 OCS, but the water from this station contained lower levels than water from RP450S. It is possible that RP0 was sampled slightly north of the discharge, at which time tidal flood currents would have moved water south in the Pass which might account for these lower levels. The data for the volatiles and PAH are positively related, thus suggesting a common source.

10.3.2 Radionuclides

Pb-210: Pb-210 activities in near-bottom waters were highest at station RP450S with an activity of $0.96 \text{ dpm}\cdot\text{l}^{-1}$, about 9 times greater than natural levels (Figure 10.6, Table F.4). Pb-210 activities elsewhere in the study area were lower (0.23 to $0.41 \text{ dpm}\cdot\text{l}^{-1}$), levels of 2 to 4 times greater than natural water Pb-210 activities.

Radium: In all water samples, U-238 and Th-234 activities were below detection levels (<0.5 and $<0.8 \text{ dpm}\cdot\text{l}^{-1}$, respectively). This lack of enhanced uranium and thorium activity indicates strongly that the high radioactivity levels associated with produced waters originate with the radium isotopes and is not supported by radioactive parents of radium which are higher in the decay chain. Total radium is the sum of Ra-226 and Ra-228 activities. The ratio of Ra-226/total Ra varies from site to site for produced waters, but in most cases the Ra-226 activity constitutes more than two-thirds of the total radium activity.

Total radium activities in near-bottom waters were highest at station RP1000N with an activity of $7.3 \text{ dpm}\cdot\text{l}^{-1}$, over 3 times greater than natural levels (Table F.4). Radium activities elsewhere in the study area were lower (3.1 to $5.7 \text{ dpm}\cdot\text{l}^{-1}$), but still above natural levels.

10.4 Sedimentary Characteristics

10.4.1 Grain Size Distribution

Grain size distributions at Romere Pass stations in October 1989 varied from dominantly sand to dominantly silt (Figure 10.7, Table B.1). Four stations (RP450S, RP100S, RP250N and RP550N) were all greater than 95% sand. Other stations were muddy sands with the exception of RP1000N which was over 78% silt and could be characterized as a sandy silt. There was no apparent spatial pattern to the variation in sand content between stations but as the lowest sand content occurred at the northernmost station it may be that this was the beginning of a lower energy sedimentary environment towards the distal end of the distributary. Further samples extending north of RP1000N would be required to confirm this change.

10.4.2 Total Organic Carbon (TOC)

TOC content of surface sediments in Romere Pass was low in October 1989 with all values being less than 1% (Figure 10.7). The only three stations with values greater than 0.1% were RP0, RP750N and RP1000N, and these coincided with stations having greater than 10% fine sediment. However, the massive increase in fines at RP1000N was not reflected in a much larger TOC content and RP750S, which also had >10% fine sediment, had a TOC content of 0.01%. Grain size distributions could not, therefore, account for the spatial variations in TOC content.

10.5 Sediment Contaminants

10.5.1 Hydrocarbons

10.5.1.1 Surficial Sediments

Alkylated PAH were detected in the sediments of Romere Pass at low levels at most stations (Figure 10.8, Table D.30). A maximum value of ~8,000 ppb was observed at RP750N ~200 m to the north of the RP-2 State discharge. A concentration of ~4,000 ppb was observed at RP1000N. FFPI values calculated for the sediments yielded values >0.8 at these two stations with a value of ~0.5 observed at RP550N.

Aliphatic hydrocarbon concentrations were detected at maximum values at the RP750N site and decreased both to the north and to the south. A slight increase in total HC was observed at the RP0 station near the OCS discharge.

The Romere Pass site is characterized by coarse sediments and a fairly high energy flow regime. The deposition of produced water hydrocarbons is therefore not favored. Highest values for alkylated PAH and total HC were observed 200 m to the north of the RP-2 State discharge. The origins of these materials may be this discharge or the other in the system. Low values next to the RP-2 State discharge may be due to the heavy vessel traffic at the dock at RP550N and continual resuspension of sediments.

10.5.1.2 Vertical Profiles

The vertical sediment core from RP1000N was analyzed since this station gave evidence of petrogenic contamination at the surface and was closest to the station showing the most contamination at the surface (RP750N). Data are presented in Table D.65 and shown graphically in Figure 10.9. While the surface section showed the highest levels of both alkylated PAH, 4,300 ppb, and total saturated hydrocarbons, 89,000 ppb, a subsurface maxima, nearly equal to surface levels, was noted for the 10-15 cm section for all hydrocarbons, and in the 20-25 cm

section for total hydrocarbons. FFPI values correlated well with the profiles of both alkylated PAH and total hydrocarbons and indicated that hydrocarbons in sections showing maximal concentrations were associated with a petroleum source. Alkylated PAH consisted primarily of naphthalenes, averaging 72% of total PAH, with the exception of the 30-34 cm section, which had 48% naphthalenes. The ratio R/T showed an increase in weathering of saturated hydrocarbons with depth in the core.

10.5.2 Trace Metals

The highest concentration of metals were not found at stations RP0 and RP550N adjacent to the discharges, but at RP750N, RP1000N and RP450S (Figure 10.10, Table E.14). All the metals analyzed followed the same distribution pattern. Trace metal concentrations in Romere Pass appeared to be unrelated to a specific discharge and were in the range normally found in nearshore marine sediments (Neff et al. 1989). The pattern of increasing concentrations in metals at RP750N and RP1000N was also noted with the hydrocarbon data. The source of these increases may be the produced water discharge at RP550N, but the reason for the low concentrations of metals and hydrocarbons at RP550N is unclear. Again, heavy vessel traffic at RP550N may continuously resuspend sediments.

10.5.3 Radionuclides

10.5.3.1 Surficial Sediments

Surficial sediment Pb-210 concentrations in the Romere Pass study area exhibited a general increase from south to north and ranged from 0.65 to 1.57 dpm·g⁻¹ (Figure 10.11, Table F.14). Surface sediment Pb-210 activities did not correlate with percent organic carbon content or with grain size. Surface sediment Pb-210 activities in coastal environments are typically about 2.0 dpm·g⁻¹ (range: 0.1 to 5.0 dpm·g⁻¹), depending on many factors controlling the sorption reactions (e.g., grain size, percent organic carbon, turbidity in overlying waters). The surface sediment Pb-210 activities observed at Romere Pass were at the upper limit for activities found in natural environments.

10.5.3.2 Vertical Profiles

Sediment Pb-210 activities within the upper 10-50 cm (length of the cores collected) increased or remained the same in a down-core direction (Table F.15). This is different from natural environments where Pb-210 sediment activities decrease down core due to decay, and reach a constant background level (~ 0.1 to 0.5 dpm·g⁻¹). Decreasing Pb-210 activities with depth in the core is a prerequisite for calculating sedimentation rates; since these conditions were not present, sedimentation rates could not be calculated for Romere Pass (see Section 3.6). The pattern observed in Emeline Pass indicated that Pb-210 supply to the sediments has greatly exceeded decay. Because the Pb-210 activities did not decrease to a background level in the Romere Pass cores, the inventories calculated from these cores give a minimum estimate of the Pb-210 flux to the area. The minimum Pb-210 sediment inventories ranged from 5.9 to 27.5 dpm·cm⁻², equivalent to the natural supply.

10.6 Benthic Biota

The benthic infauna of the Romere Pass study area was typical of both fresh and brackish environments. Organisms were bivalves (primarily *Mulinia* and *Corbicula*), nemertean worms, oligochaetes, and a few amphipods, polychaetes and gastropods.

A replicate from station RP450S was removed from the data set prior to statistical analyses. The sample contained high numbers of amphipods. Neither the species nor the high

numbers were representative of the other benthic samples. It is likely that the boat swung on anchor and the box core was collected from the marsh edge rather than mid-channel. Overall the number of species and number of individuals were low, as expected in a brackish-to-fresh transition environment. Most species and individuals were found at the northernmost two stations on the transect where salinities were higher (Figure 10.12, Table G.23). The southern end of the study transect was influenced by the fresh water of the Main Pass distributary of the Mississippi River. The northern end was influenced by more marine waters of Breton Sound.

There were statistical differences among stations for three of the benthic community parameters calculated (Tables 10.2, G.24). The differences were not obviously related to proximity to a discharge point or distance away, and there was considerable overlap in the station means.

The few number of stations in the study area limited the ability to find relationships with environmental parameters. None of the relationships described were strong. The number of species and number of individuals were positively related to the mud content of the sediments as well as the sediment total organic carbon content. There were also positive relationships between the number of species and number of individuals with the primary chemical constituents of the sediments (i.e., parent PAH, alkylated PAH, total PAH, total HC, Al, Zn, Ni and Ba). However, as noted above, none of the relationships were strong and there were only eight stations in the study area.

10.7 Summary

The Romere Pass treatment facilities are located on a distributary of the Main Pass of the Mississippi River. Romere Pass is influenced by fresh water from the river on its southern end and by more marine waters from Breton Sound on its northern end. The water column reflected these influences on the day of sampling in October 1989. The water column was well-mixed with a north-south gradient in salinity. Two facilities discharge a combined flow of produced waters at $20,000 \text{ bbl}\cdot\text{d}^{-1}$. No indication of a bottom water density plume was evident. Elevated near-bottom water sulfides, however, may be indicative of a produced water source. There were also elevated levels of volatiles and petrogenic PAH in some of the near-bottom water samples. Pb-210 and total radium activities were also above expected natural levels in near-bottom waters at several of the stations.

The current measurements and tidal velocity profile were incomplete for this study area because of poor weather conditions on the day of collection. During part of the tidal record, shear velocities were sufficient to entrain sediment from the bed and move it in the water column. The incomplete readings made it difficult to infer either a net flood- or ebb-directed movement of sediment. Sediments in the Pass were primarily sands with some contribution of silts and clays at a few stations.

Alkylated PAH were at low levels in the sediments at most stations. Where elevated, the FFPI values indicated a petrogenic origin. There were some higher values of aliphatic hydrocarbons. The distribution of the types and levels of sediment contaminants in the study area were related to a variety of factors that were not distributed across the study area uniformly. These included some sediment grain size differences, potential "down plume" accumulation, resuspension by bed sediments from the heavy vessel traffic, and additional sources of pyrogenic hydrocarbons.

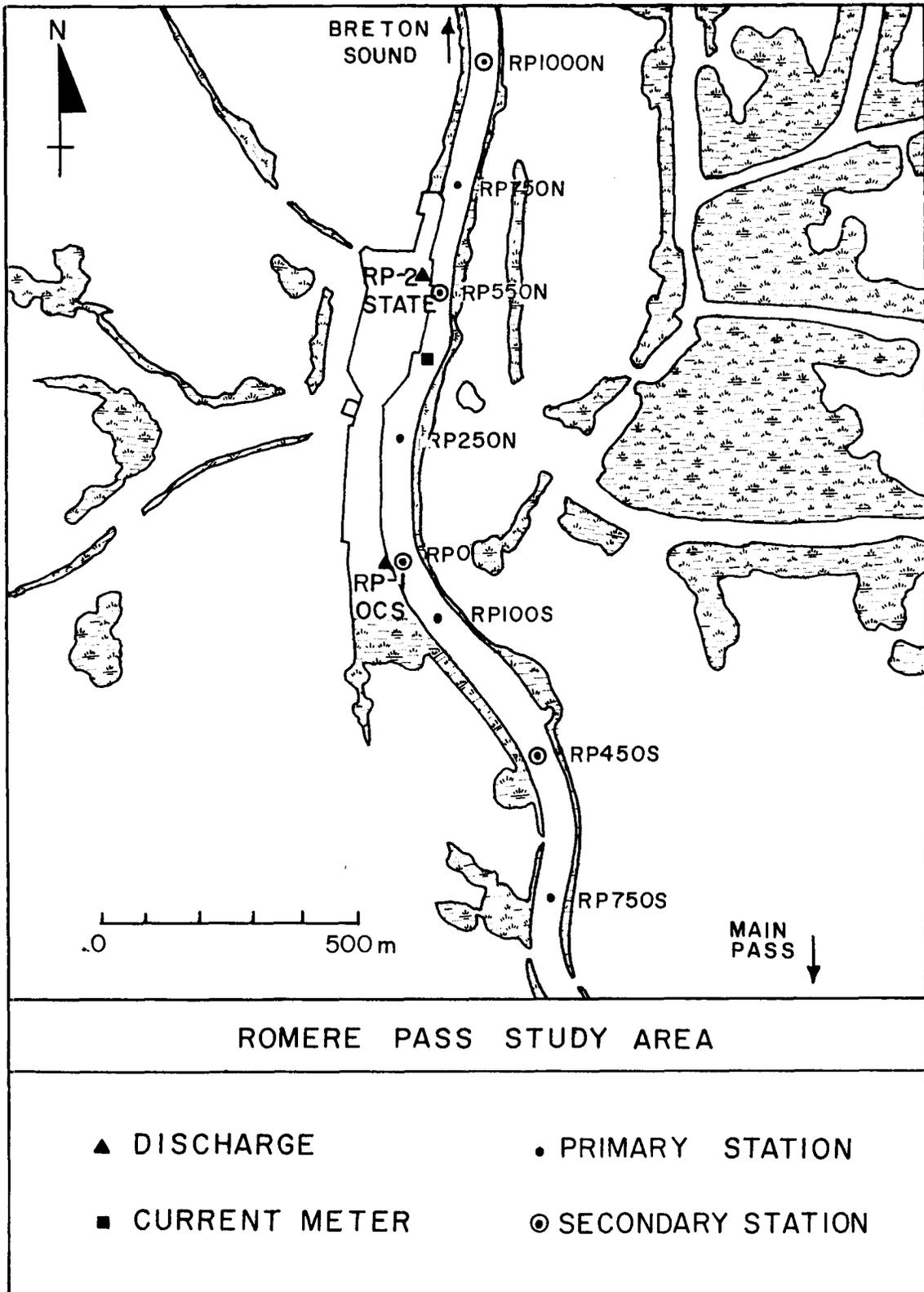


Figure 10.1. Romere Pass study area.

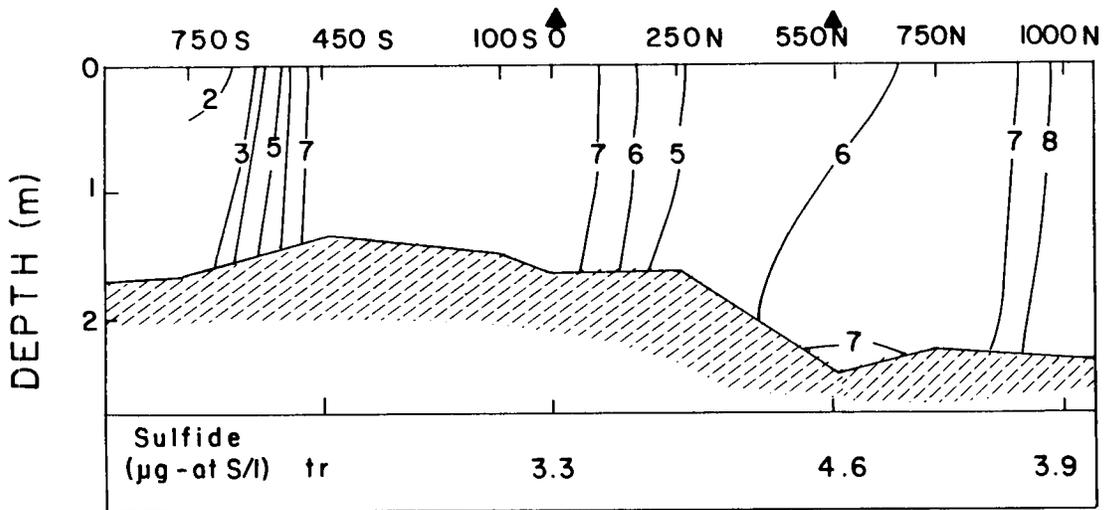


Figure 10.2. Salinity distribution through the water column and near-bottom water sulfide for selected stations at Romere Pass, October 1989. Location of discharges along axis of Romere Pass indicated by closed triangles.

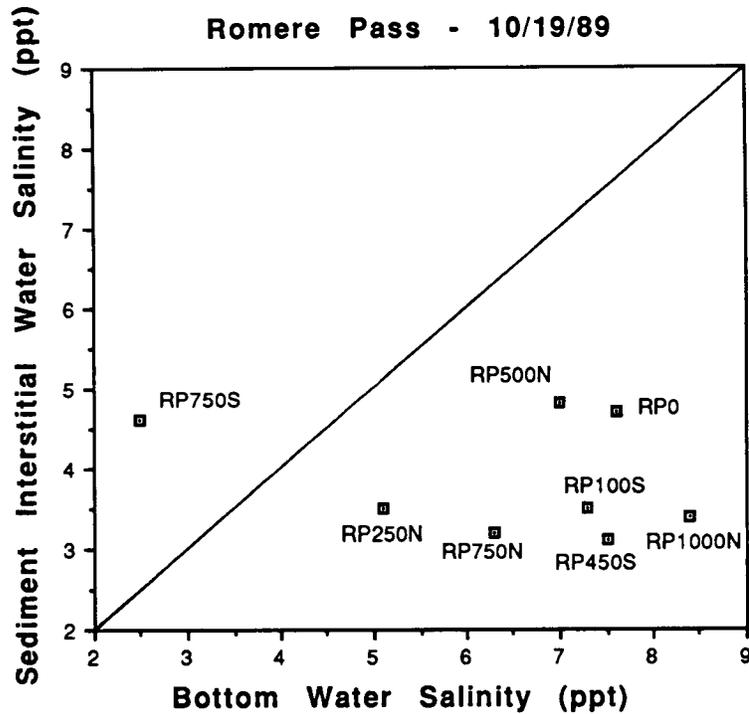


Figure 10.3. Comparisons of interstitial water salinity from surface sediments of stations in the Romere Pass study area and near-bottom water salinity. Station number given for values most different from a 1:1 relationship (indicated by diagonal line).

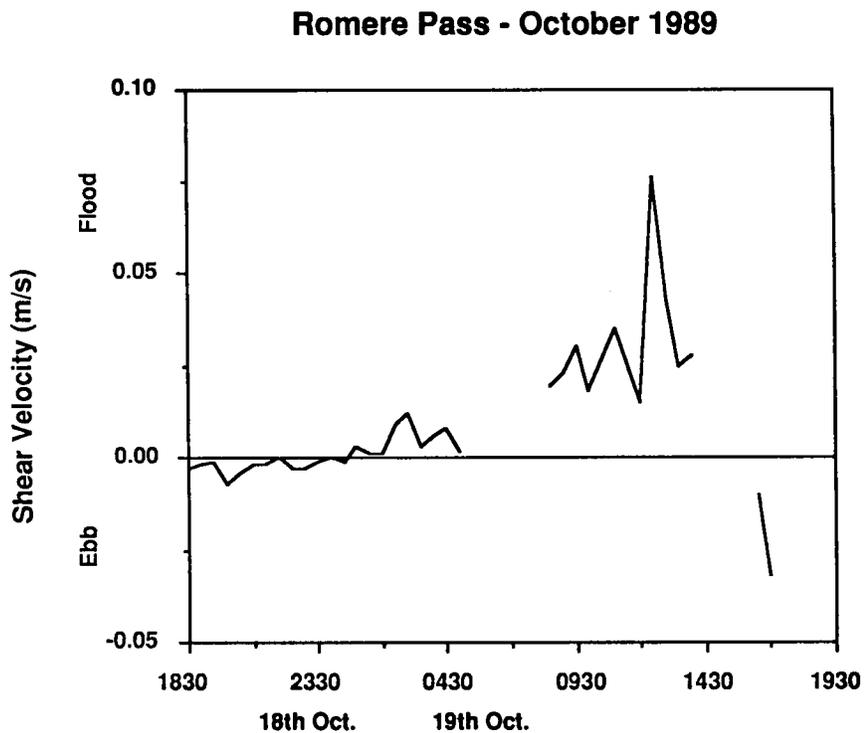
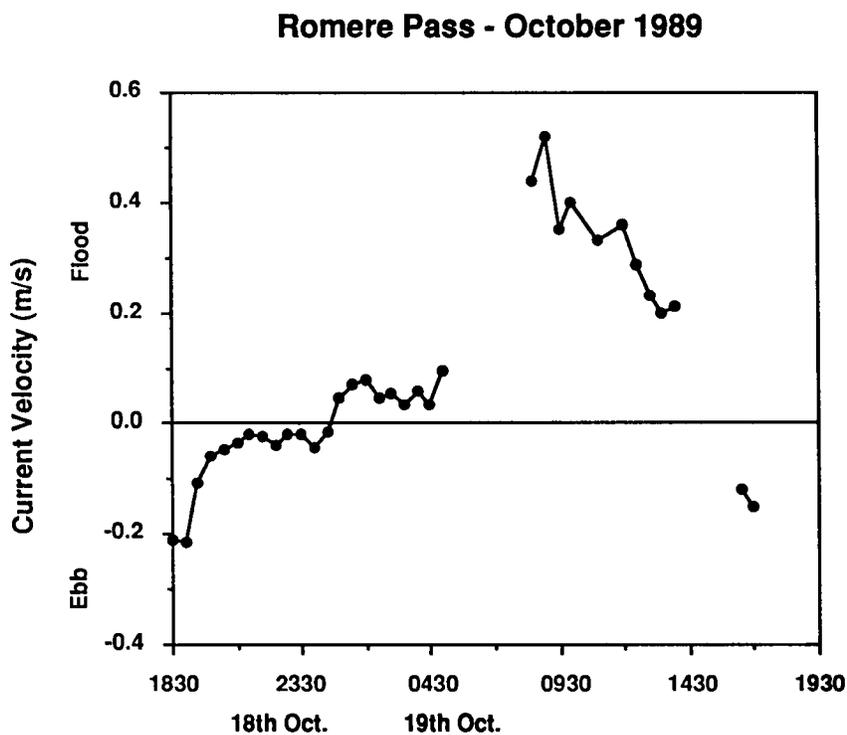


Figure 10.4. Mean tidal current velocity variation and calculated shear velocities for Romere Pass, October 1989.

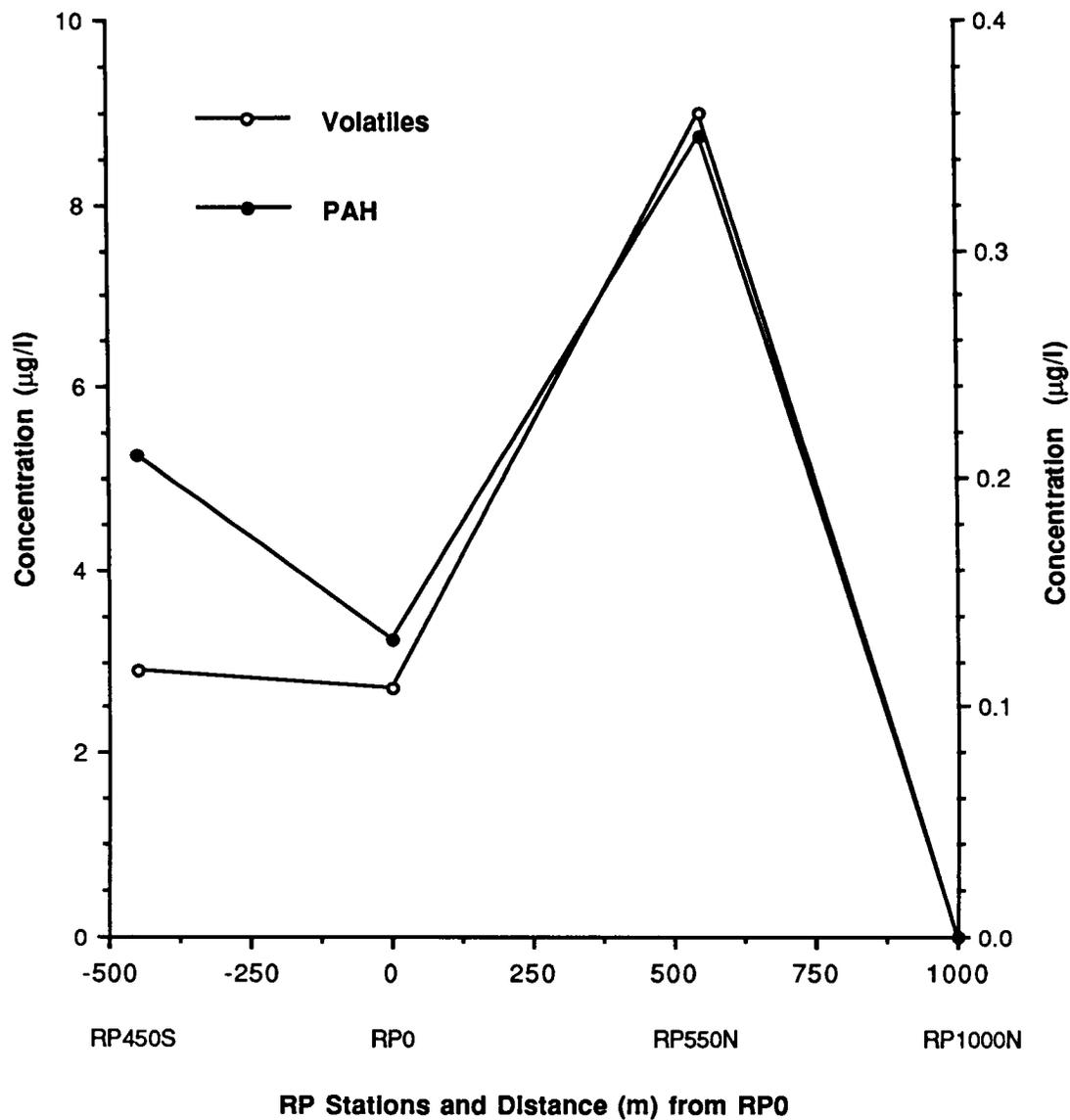


Figure 10.5. Spatial distribution of volatile hydrocarbon and PAH concentrations in Romere Pass near-bottom waters, October 1989.

ROMERE PASS: OCTOBER 1989

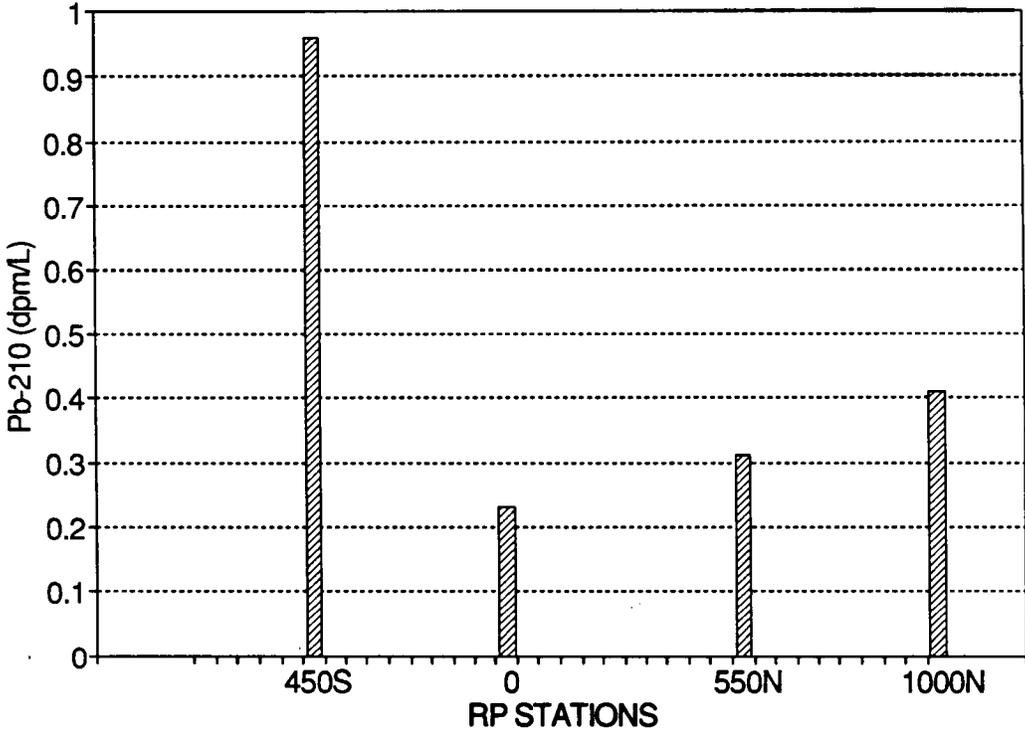


Figure 10.6. Spatial distribution of Pb-210 activities in Romere Pass near-bottom waters, October 1989.

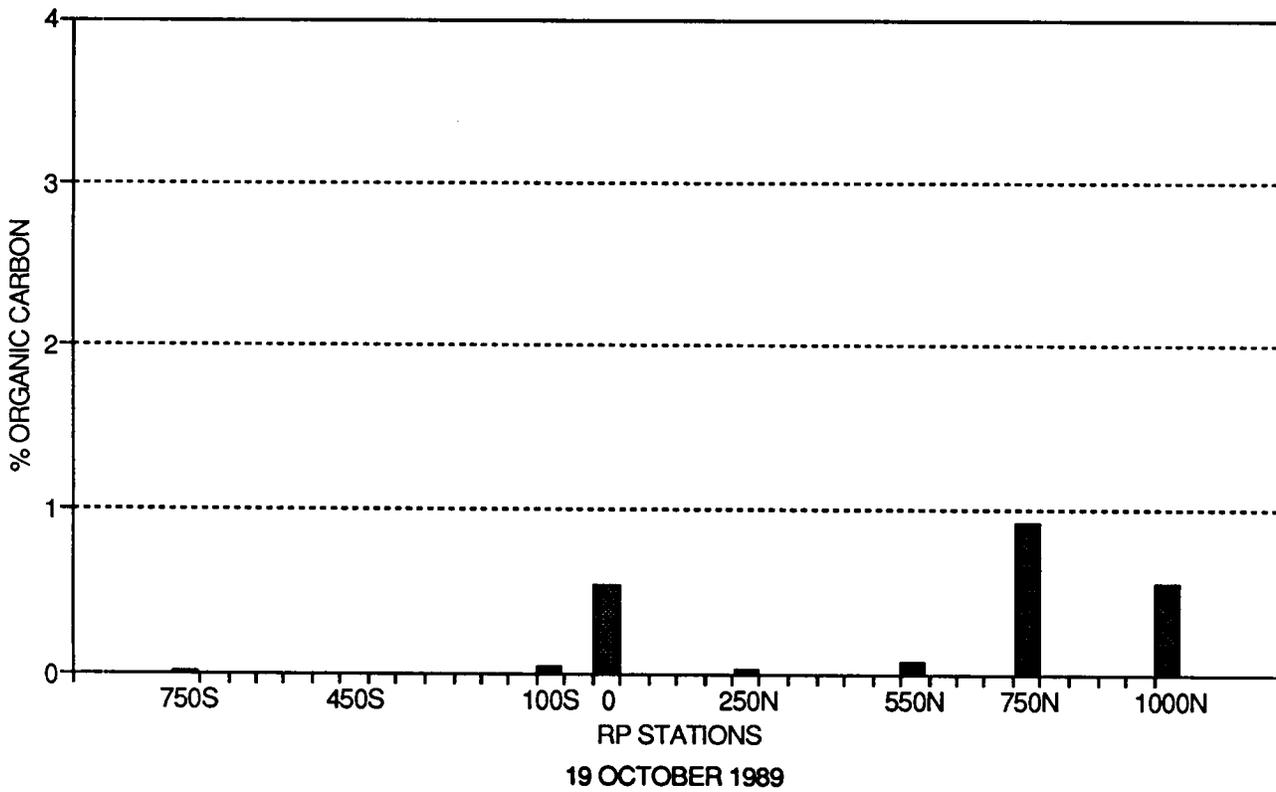
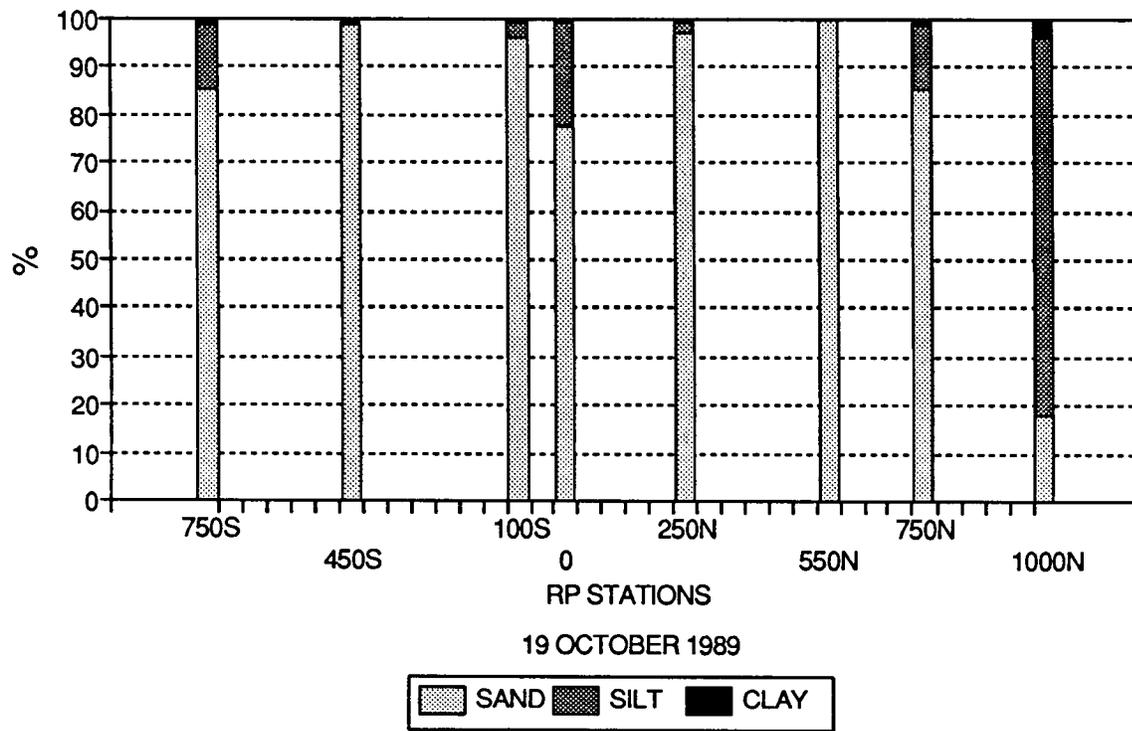


Figure 10.7. Spatial distribution of surface sediment grain size and percent total organic carbon in surface sediments from Romere Pass, October 1989.

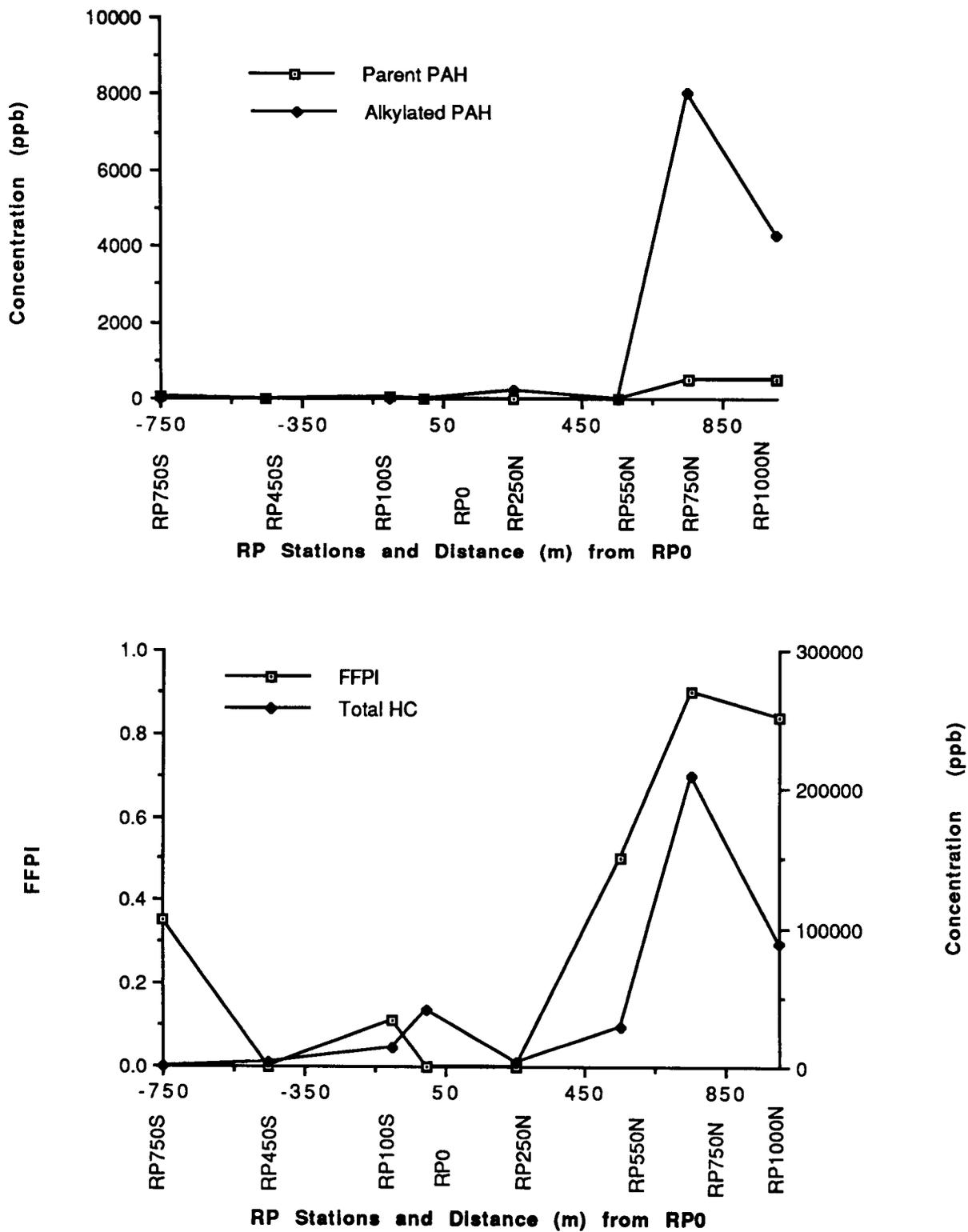


Figure 10.8. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from Romere Pass, October 1989.

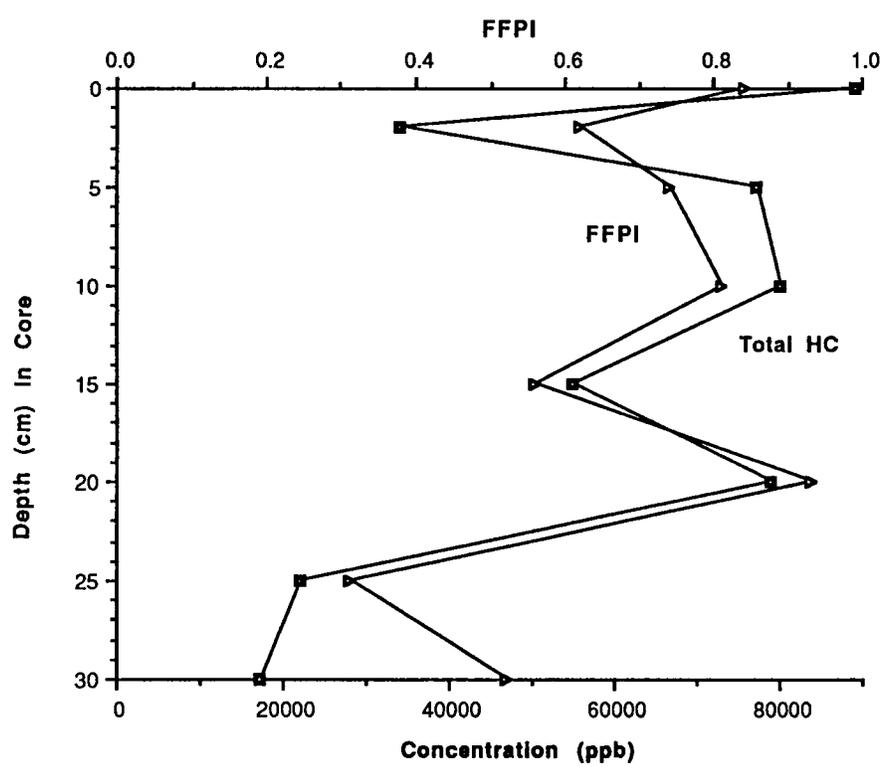
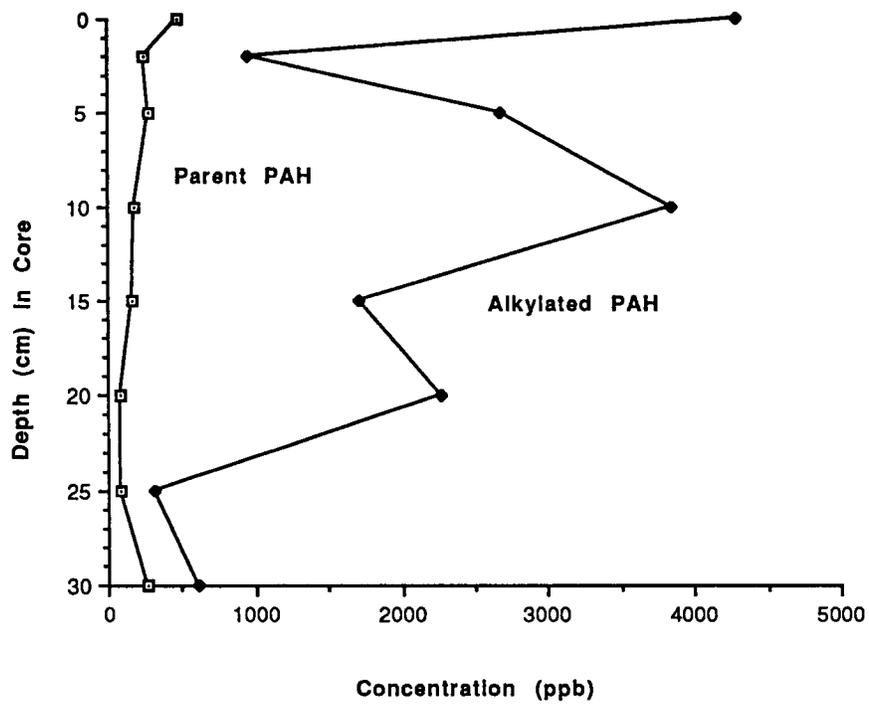


Figure 10.9. Total parent and alkylated PAH concentrations, total HC concentrations and FFPI in vertical sediment core sections from station RP1000N in Romere Pass, October 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

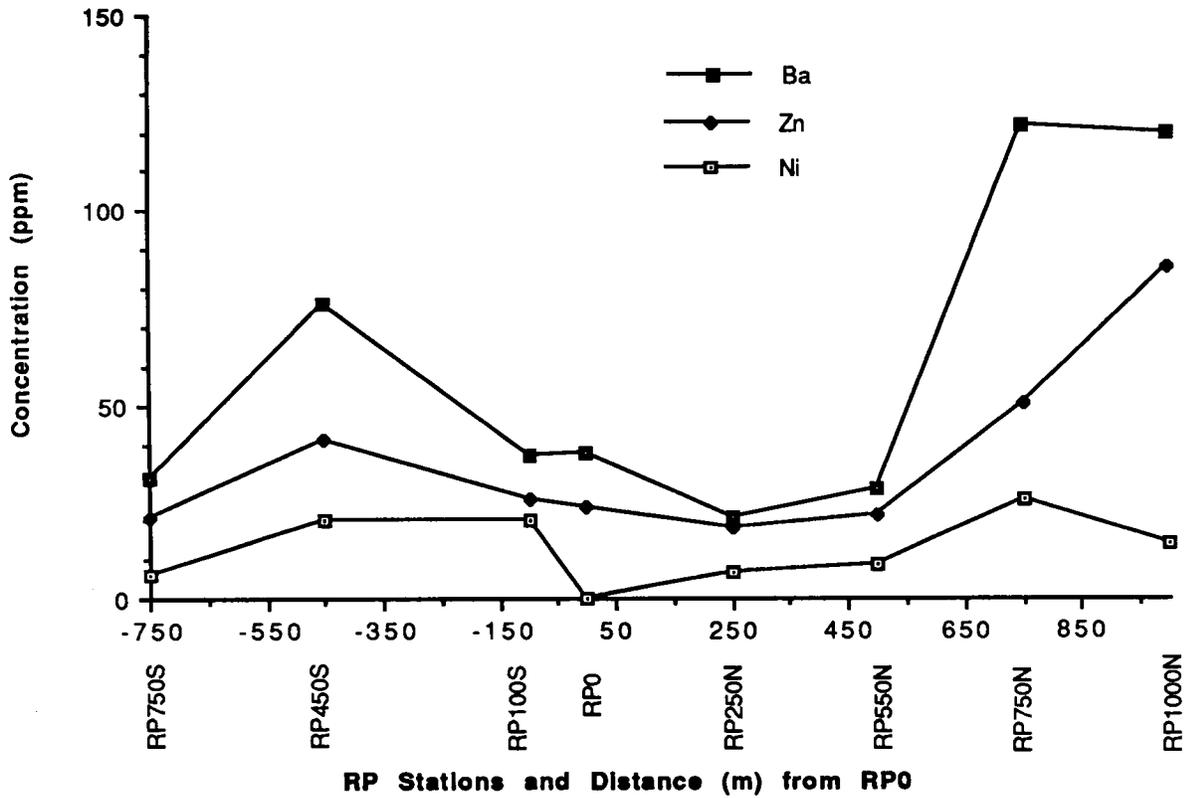


Figure 10.10. Spatial distribution of selected trace metal concentrations in surface sediments from Romere Pass, October 1989.

ROMERE PASS: OCTOBER 1989 SURFACE SEDIMENT Pb-210

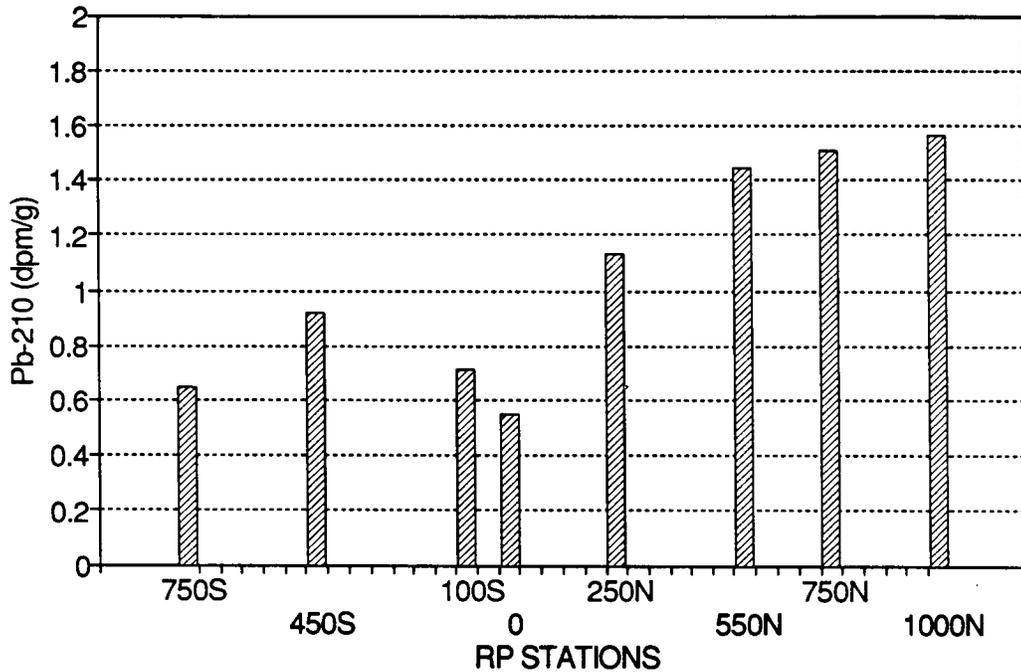


Figure 10.11. Spatial distribution of Pb-210 activities in surface sediments from Romere Pass, October 1989.

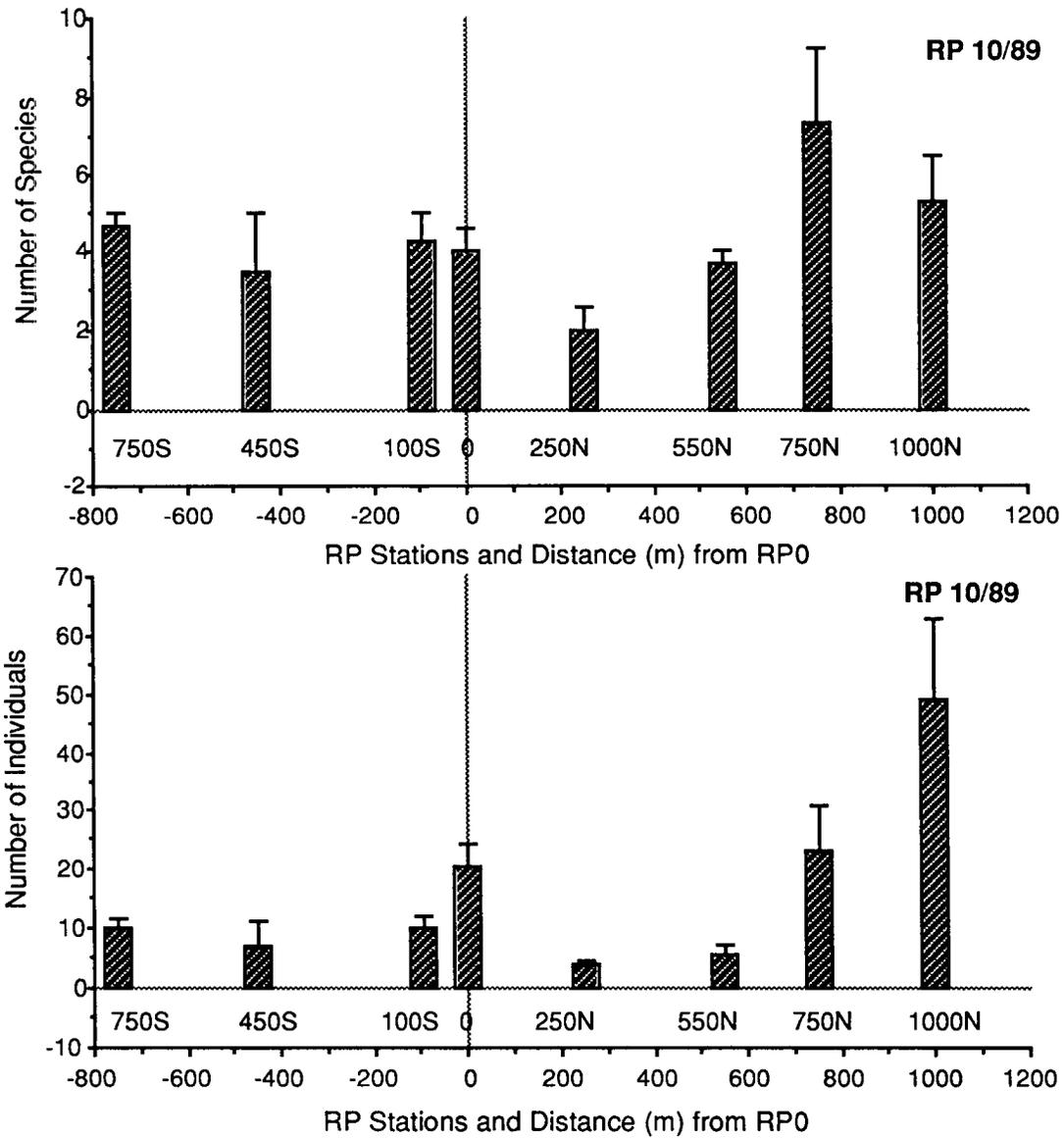


Figure 10.12. Spatial distribution of number of species per replicate (mean \pm standard error) and number of individuals per replicate (mean \pm standard error) for Romere Pass, October 1989.

Table 10.1. Comparison of average daily discharges ($\text{bbl}\cdot\text{d}^{-1}$) and oil and grease content ($\text{mg}\cdot\text{l}^{-1}$) of produced waters from facilities at Romere Pass study area. (Data provided by operators.)

Date	Facility	
	RP-1 OCS	RP-2 State
12/89		
Discharge	1,392	14,408
Oil and Grease	13	11
Average Discharge	3,021*	17,137*
Average Oil and Grease	16*	16*
Discharge Estimated in Boesch and Rabalais (1989a)	30,000	21,000
Discharge as of 03/91	5,000	20,000

*Mean of 25 monthly sample dates from 02/88 - 02/90.

Table 10.2. Duncan's multiple range test for Romere Pass study area; underlined stations are not significantly different from each other.

* Number of Species (natural log transformed):							
250N	450S	550N	0	100S	750S	1000N	750N
_____		_____		_____			
* Number of Individuals (natural log transformed):							
250N	550N	450S	750S	100S	0	750N	1000N
_____		_____		_____			
* Evenness:							
550N	750S	250N	450S	0	100S	750N	1000N
_____		_____		_____			

*Cell sizes unequal; station 450S, replicate B excluded.

Chapter 11

EMPIRE WATERWAY STUDY AREA

11.1 Description of Study Area

11.1.1 Facilities

Two facilities were the focus of studies at Empire Waterway (Figure 11.1). A single OCS produced water discharge is located on an access canal near the Empire jetties. A second facility located on another access canal nearer the Empire jetties is the site of a discontinued OCS produced water discharge. The two facilities are within 1.2 km of each other in the same general area. The dredged access canals leading to each facility averaged about 2 - 3 m water depth. They intersect Empire Waterway on their western ends and connect through natural sloughs to the salt marshes on their eastern ends. Empire Waterway is dredged to a depth of approximately 5 - 6 m. Salinities in the waterway were approximately 19 ppt and those of the access canals slightly higher. Tidal currents were strong through the Empire Waterway and into the access canals. The vegetation in the area was typical salt marsh vegetation, *Spartina alterniflora*.

The current produced water discharge facility is the Chevron Pipe Line Company West Delta 30 Terminal. The facility was acquired from Chevron U.S.A. during the Chevron-Gulf merger. The facility was constructed mainly for the purpose of treating crude oil. The facility has been in continual operation without any major interruptions since operations began in 1956. The average daily discharge rate for the facility was $10,959 \text{ bbl}\cdot\text{d}^{-1}$, based on the average of four monthly discharge rates between February 1989 and February 1990 (Table 11.1). The discharge volume for this facility estimated in Boesch and Rabalais (1989a) was $2,000 \text{ bbl}\cdot\text{d}^{-1}$ based on the permit application. The increase in volume is attributed to a greater proportion of water generated as the reserves in the field are depleted. The hydrocarbon levels of the discharge, reported as oil and grease content, averaged $26 \text{ mg}\cdot\text{l}^{-1}$ over the 25-month period from February 1988 - February 1990. The reported salinity of the discharge based on the permit application sampling was 160.8 ppt.

The treatment facility at West Delta 30 Terminal is a mixture of heat treatment and settlement. The final treatment is a separation pond which empties through a discharge pipe into a slough in the marsh adjacent to the facility. The discharge is not located in the access canal where sample stations were located. Drainage patterns from the slough and the marsh observed during the November 1989 field trip indicated that some of the effluent would possibly flow into the channel adjacent to the facility.

The West Delta 30 Terminal is scheduled to be shut down by August 1992. The facility will be removed and the pits closed. A small pipeline valve station will remain at the site.

The Exxon Co., USA Pelican Island Terminal is no longer in operation, and, at the time of the field studies, was in the process of being dismantled. When discharging, the volume reported was 12,000 to $15,000 \text{ bbl}\cdot\text{d}^{-1}$ (Table 11.1). The facility began operations in 1956 and continued to July 1987. Between the date of the aerial photographic mission in November 1988 and the field collections in November 1989, most of the facility structures had been removed. Work was in progress on closing the pits and restoring the land. The design of the Pelican Island Terminal, as derived from aerial photographs, was similar to that of the West Delta 30 Terminal, with a series of heat treaters, separation tanks and pits. The discharge for the Pelican Island Terminal also appeared to have been from a pipe near a slough in the marsh, with possible

movement of the discharge into the access canal. Produced waters that were once handled by the Pelican Island Terminal are now handled by the Exxon Grand Isle facility.

11.1.2 Study Design

For each of the facilities, a series of stations were situated along the access canals in similar distances away from the point where the discharge (or the discontinued) discharge was expected to enter the channel (Figure 11.1). Additional stations were placed in Empire Waterway adjacent to each of the access canals. Stations EW2 and EW11 had to be relocated from the positions originally intended based on distance from the discharge. The bottom was shell hash which originated from pipeline crossings or shoreline rip-rap and was difficult to penetrate. Station EW5 could not be sampled because of shrimp boats anchored across the channel east of the Pelican Island Terminal. A barge with sediment to be used in the restoration of the Pelican Island facility was anchored in the channel next to station EW3, and we had to position the station to avoid sampling sediments that had washed off of it. Sampling was conducted in November 1989.

The data for the Empire Waterway study site are plotted as a function of distance away from the point of produced water discharge (or abandoned discharge) in the marsh. In the case of the Pelican Island Terminal, the point of the abandoned discharge was surmised from the aerial photographs and discussions with representatives of Exxon Pipeline Company. Two transects are plotted; one in reference to the current discharge (Stations EW6 through EW11) and a second in reference to the abandoned discharge (Stations EW1 through EW6). Station EW6 was common to both transects for intercomparison.

11.2 Hydrography

11.2.1 Hydrographic Profiles

The salinity profiles for the stations sampled in Empire Waterway and the facilities' access canals indicated that the water column was well-mixed with the exception of EW4 (Figure 11.2, Table A.15). Salinities in Empire Waterway were approximately 19 ppt. There was a slightly higher water column salinity at one station in Empire Waterway (21 ppt for EW2) and in both of the access canals (20 ppt at EW3 and EW4 for the Pelican Island facility, and 21 ppt at EW8, EW9 and EW10 for the West Delta 30 Terminal). The low salinity in the surface water for EW4 (10.9 ppt) is thought to be real (rather than equipment malfunction or sampling error), because the salinity at 0.5 m was also reduced below that of the ambient salinity. The reason, however, remains unexplained but may be related to localized freshwater run off associated with some operation of the facility removal or previous heavy rainfall. Water temperatures were 22 to 23°C. The water column was well-oxygenated at all stations. Sulfide levels in near-bottom waters were trace or not detected except for one station (sulfide = $3.9 \mu\text{g-at S}\cdot\text{l}^{-1}$ at EW7) (Table A.15).

11.2.2 Dispersion of Effluent

The salinity of the produced water discharge at the West Delta 30 Terminal was 140.5 ppt. An effluent density plume of the produced water discharge was not evident from the water column CTD casts in the access canal or in Empire Waterway. The actual direction of dispersion of the effluent is not clear since the discharge pipe is located in the marsh along a slough. There is no produced water discharge at the abandoned Pelican Island facility.

The interstitial salinity of surficial sediments collected from box cores were not unusually elevated above the ambient levels (Figure 11.3). The elevated salinity of interstitial waters in surficial sediments indicated prior exposure to higher salinities than detected in the water column

on the day of sampling. Salinities of 23 to 26 ppt (those of the interstitial water) would not be unexpected for this area. There were also no consistent trends with higher interstitial water salinities for stations located closer to the discharge.

The sulfide concentration of the produced water discharge at the West Delta 30 Terminal was $6.5 \mu\text{g-at S}\cdot\text{l}^{-1}$. Sulfide levels of $3.9 \mu\text{g-at S}\cdot\text{l}^{-1}$ at station EW7 could possibly be related to the effluent; however, stations closer to the discharge (EW8 and EW9) did not have elevated levels of sulfide in the bottom waters.

11.2.3 Tidal Current Regime

Velocity monitoring at Empire Waterway was conducted during a high spring tide with a predicted range of 2.3 ft at Empire Jetties. An anchor station was maintained for 25 hours in an access canal off the main waterway, close to station EW9. Monitoring began during the ebb tide as mean velocities were beginning to decrease (Figure 11.4). There was a slight asymmetry with maximum mean ebb velocities of over $0.75 \text{ m}\cdot\text{s}^{-1}$ while the flood maximum reached $0.72 \text{ m}\cdot\text{s}^{-1}$. The pattern is that of a typical diurnal tide with a 12.5-hr flood cycle and a similar duration for the ebb.

11.2.4 Velocity Profiles

Shear velocity values calculated from the velocity profiles for Empire Waterway showed a similar ebb and flood pattern to the mean velocities (Figure 11.4). There was a more pronounced asymmetry with higher shear velocities on the ebb, reaching almost $0.05 \text{ m}\cdot\text{s}^{-1}$. Comparison of the data showed that maximum shear velocity did not coincide with maximum mean velocity, with the highest shear occurring near the beginning of the flood and the ebb. There was clear potential for sediment entrainment in this canal during both flood and ebb tides. However, it is important to note that these measurements were taken during a high spring tide and so may reflect higher bed shear stresses than occur throughout most of the year in this location.

11.3 Water Column Contaminants

11.3.1 Hydrocarbons

The data for near-bottom water samples are presented in Table D.15. None of the samples analyzed contained detectable levels of either volatile hydrocarbons or PAH. There were low levels of saturated hydrocarbons detected in all samples, which were probably from natural sources and not related to the discharge. This is based on composition of the saturates which were high molecular weight hydrocarbons ($> \text{nC-25}$), typical of the hydrocarbon patterns derived from plant waxes.

11.3.2 Radionuclides

Pb-210: Pb-210 activities in near-bottom waters were highest at station EW3 with an activity of $0.35 \text{ dpm}\cdot\text{l}^{-1}$, about 3 times greater than natural levels (Figure 11.5, Table F.4). Pb-210 activities elsewhere in the study area ranged from 0.07 to $0.18 \text{ dpm}\cdot\text{l}^{-1}$, within the usual range of natural water Pb-210 activities.

Radium: In all water samples, U-238 and Th-234 activities were below detection levels (<0.5 and $<0.8 \text{ dpm}\cdot\text{l}^{-1}$, respectively). This lack of enhanced uranium and thorium activity indicates strongly that the high radioactivity levels associated with produced waters originate with the radium isotopes and is not supported by radioactive parents of radium which are higher in the decay chain. Total radium is the sum of Ra-226 and Ra-228 activities. The ratio of

Ra-226/total Ra varies from site to site for produced waters, but in most cases the Ra-226 activity constitutes more than two-thirds of the total radium activity.

Total radium activities in near-bottom waters were highest at station EW9 with an activity of $92 \text{ dpm}\cdot\text{l}^{-1}$, about 45 times greater than natural levels (Table F.4). Radium activities elsewhere in the study area ranged from 65 to $81 \text{ dpm}\cdot\text{l}^{-1}$, above natural levels 32 to 40 times.

11.4 Sedimentary Characteristics

11.4.1 Grain Size Distribution

Grain size distributions in surface sediment samples at all Empire Waterway stations were dominated by silts (>60% at all sites). Clay content was typically between 2% and 10% (Figure 11.6, Table B.1). Sand content varied between 30% at EW11 and 8% at EW1. Both of these sites were in the main Empire Waterway channel but the channel appeared to have no clear influence on grain size characteristics. Similarly, neither of the access canals east of the main channel showed any characteristic grain size distribution.

11.4.2 Total Organic Carbon (TOC)

The TOC content of surface sediments of the Empire Waterway samples varied between 3.32% at EW10 to 1.25% at EW1 (Figure 11.7, Table B.1). The highest value was at the head of the northern access canal and close to the marshes. This may account for the high values with organic debris from the salt marshes being incorporated into the sediments. Variations between other stations showed no clear spatial pattern. The main Empire Waterway channel showed no influence on TOC content of sediments with both high and low values being found at channel stations. The increase in TOC at the head of the northern access channel was not found in the southern access canal (EW3 and EW4); however, a station located physiographically similar to EW10 was not possible in the southern canal.

11.5 Sediment Contaminants

11.5.1 Hydrocarbons

11.5.1.1 Surficial Sediments

No significant levels of alkylated PAH were detected in any of the sediments along the transect near the current discharge (Figure 11.8, Table D.31). Parent PAH were detected at most stations at levels usually associated with background (<50 ppb). A maximum parent PAH level was observed at the EW9 station fairly close to the separation facility and may be associated with diesel exhaust from compressors, pumps and other machinery at that location or supply vessels. All values of FFPI along the transect adjacent to West Delta 30 Terminal were <0.05, indicating no input of petrogenic hydrocarbons.

Total hydrocarbons were detectable at all stations along the transect but were maximal at the EW6 site far away from either the current discharge or the abandoned discharge.

In contrast to the active discharge, alkylated PAH near the abandoned discharge, were detected at low concentrations at several stations along the transect (Figure 11.9). The maximum value was observed at EW4, ~200 m from the Pelican Island facility. Alkylated PAH concentrations decreased away from this point. Parent PAH were also detected at similar levels in the sediments at most stations along the transect near the Pelican Island facility. FFPI values calculated for these sediments yielded values ~0.5 for the stations where alkylated PAH were

detected at higher levels, and <0.05 at all other stations. This was consistent with the parent PAH concentrations observed along this transect.

Total hydrocarbon concentrations in sediments of the two transects were similar. The maximum level detected was at station EW6 (the linking station between transects); however, a gradient of total HC concentrations was observed with distance away from the Pelican Island abandoned facility. A total HC level of ~36,000 ppb was observed at EW4 near the abandoned discharge.

11.5.1.2 Vertical Profiles

Vertical sediment cores from stations EW2, EW3 and EW4 near the abandoned discharge site, were analyzed because these stations showed the only petrogenic contamination in surface sections from this study area. Other sections showed only pyrogenic contamination as indicated by low FFPI values. In general, concentrations of petroleum-source hydrocarbons were relatively low compared to other study areas, and concentrations were maximal either at the surface (0-2 cm) or the 2-5 cm section. Data for the vertical cores are detailed in Tables D.66 - 67 and shown in Figure 11.10.

EW2: The profiles for this core showed surface maxima of alkylated PAH (Figure 11.10), total HC and FFPI, thereafter levels were trace or not detected for PAH; total HC averaged 3,900 ppb. FFPI showed a high value of 1.0 in the 2-5 cm section, due to the presence of naphthalene as the only PAH detected. R/T values were also erratic due to the low concentrations of HC, and probably reflected plant inputs.

EW3: Alkylated PAH were detected only in the 2-5 cm and 15-20 cm sections of this core and averaged 200 ppb. Total HC showed the same subsurface rise in the 2-5 cm section, and a second increase at 20-25 cm, and averaged 7,500 ppb. The only FFPI value, 0.27 at 2-5 cm, was low, indicating that the majority of hydrocarbon contaminants present in this section were not of petrogenic origin. R/T values were 0.30 at the surface and 1.0 from 5-20 cm, due to the absence of an unresolved complex, indicating that hydrocarbon concentrations were influenced by plant inputs.

EW4: The 2-5 cm section from this station showed the highest concentration of alkylated PAH, 1,900 ppb, and total HC, 67,000 ppb, of that observed in Empire Waterway cores studied, as well as all surface sections. Concentrations generally decreased with depth, except for a rise in alkylated PAH at 20-25 cm. Parent PAH concentrations were higher in sections nearer to the surface and at a stable level in the bottom half of the core. FFPI was highest for the 5-10 cm section, 0.70, and again at 20-25 cm, 0.61, the pattern corresponding with that of the alkylated PAH. R/T values averaged 0.04 in the top four sections, then rose to a high of 0.18 in the bottom section, where low concentrations probably reflected plant inputs to resolved HC. Naphthalenes, when detected, averaged 28% of total PAH, phenanthrenes averaged 40% and fluorenes averaged 42% where detected. These values were lower for naphthalenes and higher for the phenanthrenes and fluorenes than that found in other study areas, but may be a reflection of the generally low concentration of all PAH.

11.5.2 Trace Metals

11.5.2.1 Surficial Sediments

Figure 11.11 and Table E.15 present the trace metal data for surface sediments. Trace metal concentrations were generally low with the maximum values grouped near the two facilities. Metals displaying similar distribution patterns were Al, Cr, V, Zn, Ba and Pb. It appeared from these data that the discharges in this area have added low amounts of some metals

to the sediments. The distribution pattern of hydrocarbons differed from what was observed with the metals data.

11.5.2.2 Vertical Profiles

Vertical sediment cores from stations EW2, EW3 and EW4 were analyzed for trace metals (Tables E.27 - E.29 and Figure 11.12). Again, trace metal concentrations in general did not appear similar to the patterns from hydrocarbon data. In general concentrations were low compared to those found in vertical core sections at other study sites. The highest concentration observed in the three cores was for the 20-25 cm section of EW3, 250 ppm Ba. This value was also higher than for any of the surface sections from all stations. Barium values in the EW3 core generally increased from a minimum at 5-10 cm. Other trace metals observed in this core did not follow this pattern. The core from EW4 showed a similar pattern for Ba, Zn and V concentrations, with maximal values in the 2-5 cm or 5-10 cm and 25-30 cm sections, and minimal values at the surface and central sections of the core. The maxima observed in the 2-5 cm and 5-10 cm sections coincides with maximal alkylated PAH and total HC concentrations.

11.5.3 Radionuclides

11.5.3.1 Surficial Sediments

Surficial sediment Pb-210 concentrations in the Empire Waterway ranged from 1.10 to 2.80 dpm·g⁻¹ during November 1989 (Figure 11.13, Table F.13). There was a positive relationship of Pb-210 activities to the clay content of the sediments, but no clear relationship with sediment organic content. Surface sediment Pb-210 activities in coastal environments are typically about 2.0 dpm·g⁻¹ (range: 0.1 to 5.0 dpm·g⁻¹), depending on many factors controlling the sorption reactions (e.g., grain size, percent organic carbon, turbidity in overlying waters). The surface sediment Pb-210 activities observed at Empire Waterway are at the upper limit for activities found in natural environments.

11.5.3.2 Vertical Profiles

Sediment Pb-210 activities within the upper 10-50 cm (length of the cores collected) increased or remained the same in a down-core direction (Table F.15). This is different from natural environments where Pb-210 sediment activities decrease down core due to decay and reach a constant background level (~ 0.1 to 0.5 dpm·g⁻¹). Decreasing Pb-210 activities with depth in the core is a prerequisite for calculating sedimentation rates; since these conditions were not present, sedimentation rates could not be calculated for Empire Waterway (see Section 3.6). The patterns observed in the Empire Waterway site indicated that Pb-210 supply to the sediments has greatly exceeded decay. Because the Pb-210 activities do not decrease to a background level in cores, the inventories calculated from these cores give a minimum estimate of the Pb-210 flux to the area. The minimum Pb-210 sediment inventories ranged from 18.2 to 76.8 dpm·cm⁻², representing 1.0 to 2.4 times the natural Pb-210 supply.

11.6 Benthic Biota

The benthic infauna of the Empire Waterway study area was a combination of marine and intermediate salinity organisms, primarily polychaetes. The dominant polychaetes were *Paraprionospio pinnata* in Empire Waterway stations and *Mediomastus ambiseta* at stations in the facility access canals. There were several other species of polychaetes, oligochaetes, nemertean worms, bivalves, gastropods, ophiuroids and decapod crustaceans. Because of the variety of habitats in the study area, the total number of species was high. For any single station, however, the number of species averaged 10 to 15 per replicate (Table G.25).

The Empire Waterway study area had two facilities. One facility was a current discharge near stations EW8 and EW9. The second facility was an abandoned discharge near station EW4. For consideration of differences in the benthic fauna related to each of these facilities, the data were divided into those stations closest to each facility with overlap in the data for station EW6. The statistical analyses (Tables G.26 and G.27) and data presentations reflect this division (Figure 11.14, Tables 11.2 - 11.3).

For those stations in the northern part of the study area near the current discharge, there were no statistical differences among stations in the number of species, but there were differences in number of individuals, diversity and evenness (Table G.26). The differences, however, were not related to distance from the discharge point. In fact, stations EW8 and EW9, the two stations closest to the discharge point were consistently different from each other with regards to all the statistically significant benthic community parameters (Table 11.2).

For those stations in the southern part of the study area near the abandoned discharge, there were statistically significant differences among stations in number of species, number of individuals and diversity (Table G.27). Station EW4, nearest the abandoned discharge, had the lowest number of species and individuals (Figure 11.14 and Table 11.3). It was not, however, different in these parameters from station EW1 at the southern reach of the Empire Waterway. Station EW3 closest to EW4 differed from it with regards to both number of species and number of individuals.

There were no relationships between the number of species and number of individuals and sediment grain size and total organic content. The sediments, however, were uniformly composed of a majority of silts and TOC values were generally 2% for most samples.

Similarly, there were no relationships of the benthic fauna with most of the sediment contaminants. Concentrations in the sediments, however, were generally low throughout the study area. There was a pronounced decrease in number of species and number of individuals at station EW4 near the abandoned Exxon discharge site. These reductions were related to elevated levels of alkylated PAH above 60 ppb. The vertical core for this station also indicated an accumulation of petrogenic HC subsurface and at depth.

11.7 Summary

The Empire Waterway study area has two facilities with very similar treatment methods and location configurations. Both are located on dredged access canals which join Empire Waterway. The final treatment at both facilities was a holding pond from which the produced water effluent entered a slough in the adjacent marsh. One of these facilities (West Delta 30 Terminal) was discharging produced waters at a rate of 11,000 bbl·d⁻¹ during the field studies, but the second stopped discharging an average of 12,000 to 15,000 bbl·d⁻¹ in 1987 and the facility is being dismantled and the land restored. Water depths in the access canals were 2-3 m and that of Empire Waterway was 5-6 m.

The stations studied around each discharge were also similar in several characteristics. Sediments were predominantly silts at all of the stations, and the total organic carbon content was generally 2%. The water column was well-mixed at most stations, and there was no indication of elevated salinities or a produced water plume in the bottom waters. Current velocity measurements were made near station EW9 but were thought to be similar for both access canals. Current measurements and calculated shear velocity values indicated a clear potential for sediment entrainment in the canal during both flood and ebb tides. There was also an asymmetry in the pattern with higher velocities reached on the ebb tide. These

measurements, however, were taken during a high spring tide and may not be completely representative of bed shear stresses that occur through most of the year.

There were no detectable levels of volatile hydrocarbons or PAH in any of the near-bottom water samples. Saturated hydrocarbons were low, and Pb-210 activities were within natural levels. The total radium activities in bottom waters, however, exceeded natural levels 32 to 40 times.

No significant levels of alkylated PAH were detected in any of the sediments along the transect near the current discharge. Pyrogenic hydrocarbons were detected at EW9 where the docking facilities for the terminal are located. On the other hand, alkylated PAH were detected at low concentrations at several stations along the transect near the abandoned discharge. The maximum value was located close to the discharge point and decreased away from there. FFPI values indicated a petrogenic source for the sediments with elevated PAH. Trace metals concentrations for surface sediments were generally low with higher values being found near the facilities.

Analyses of vertical sediment cores from the transect near the abandoned discharge revealed the highest concentrations of alkylated PAH and total HC for the study area; these were in the subsurface (2-5 cm) and deeper (20-25 cm) sections of the core at EW4. Other peaks in hydrocarbons were also found in subsurface and deeper sections of vertical cores at EW3 and EW2, but not to the degree as found at EW4. Cores were not analyzed from the transect adjacent to the current discharge because of the low concentrations and nature of the hydrocarbons in those surface sediments. Data from the vertical cores at the abandoned discharge point to the continued accumulation and subsequent persistence of produced water-associated hydrocarbons for at least four years after the effluent was stopped.

There were no obvious impacts to the benthic fauna with the exception of station EW4 near the abandoned discharge, where the number of species and number of individuals were reduced. These reductions were associated with higher levels of alkylated PAH and total HC in the surface, and probably subsurface, sediments.

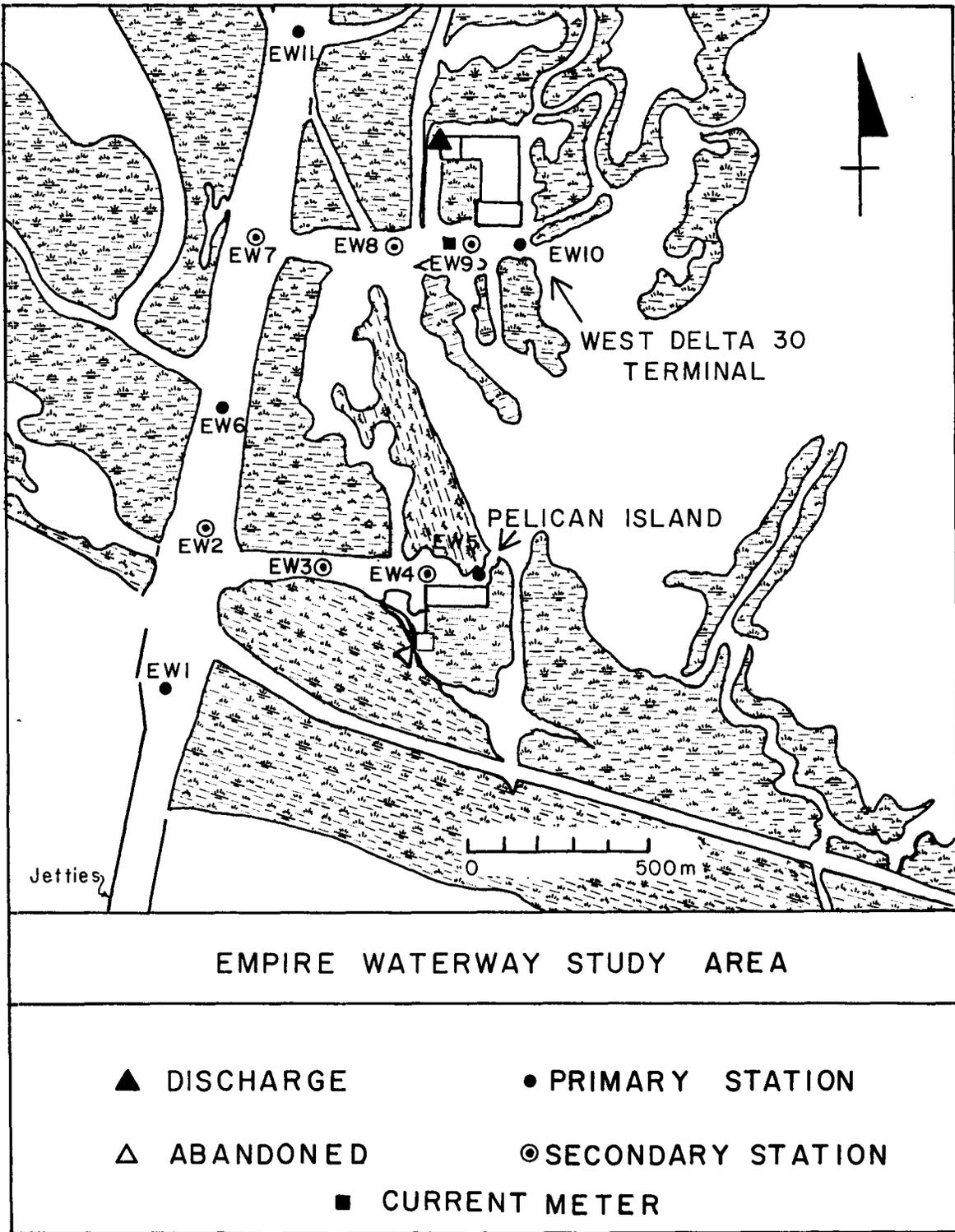


Figure 11.1. Empire Waterway study area.

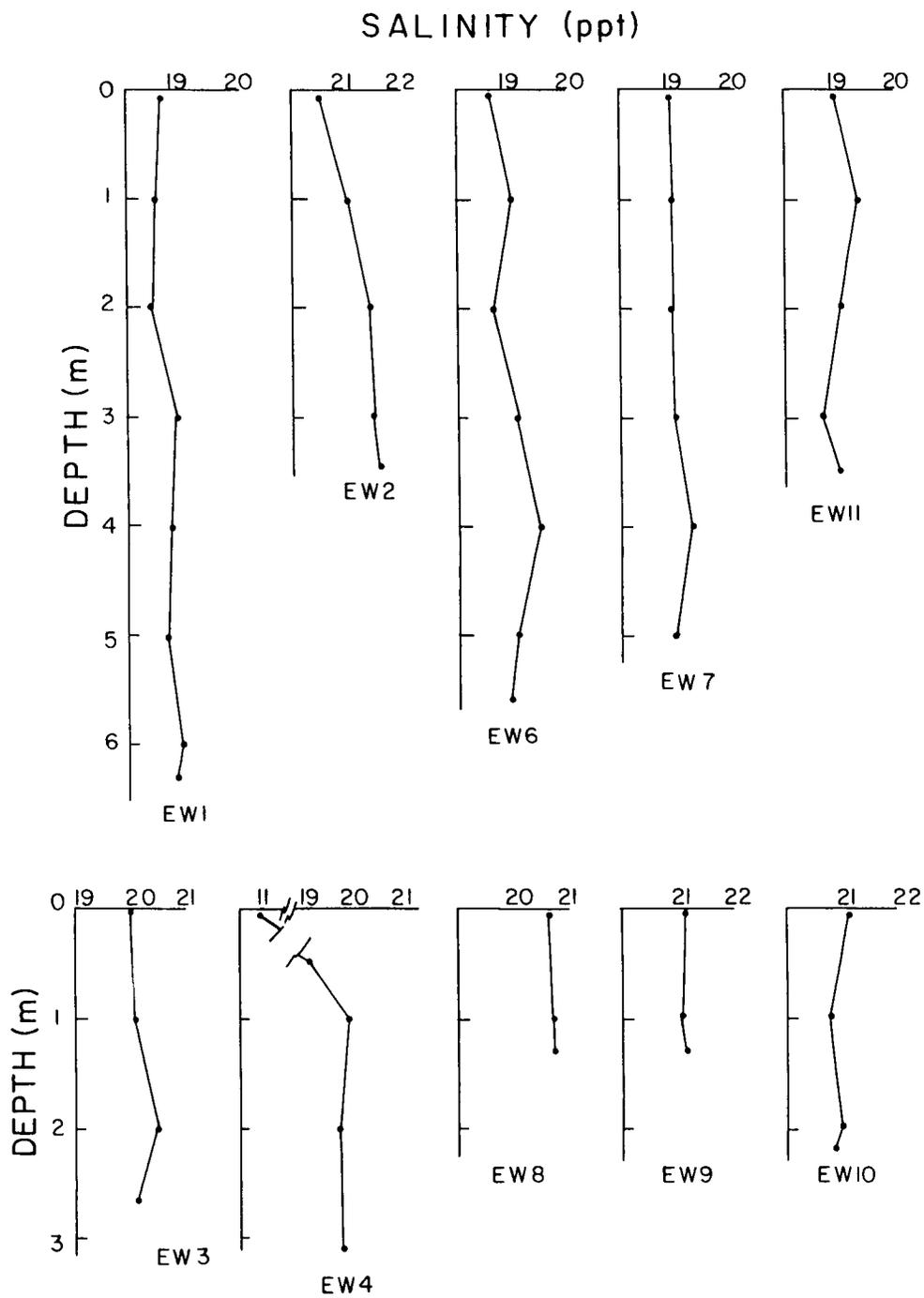


Figure 11.2. Salinity distribution through the water column for selected stations at Empire Waterway, November 1989.

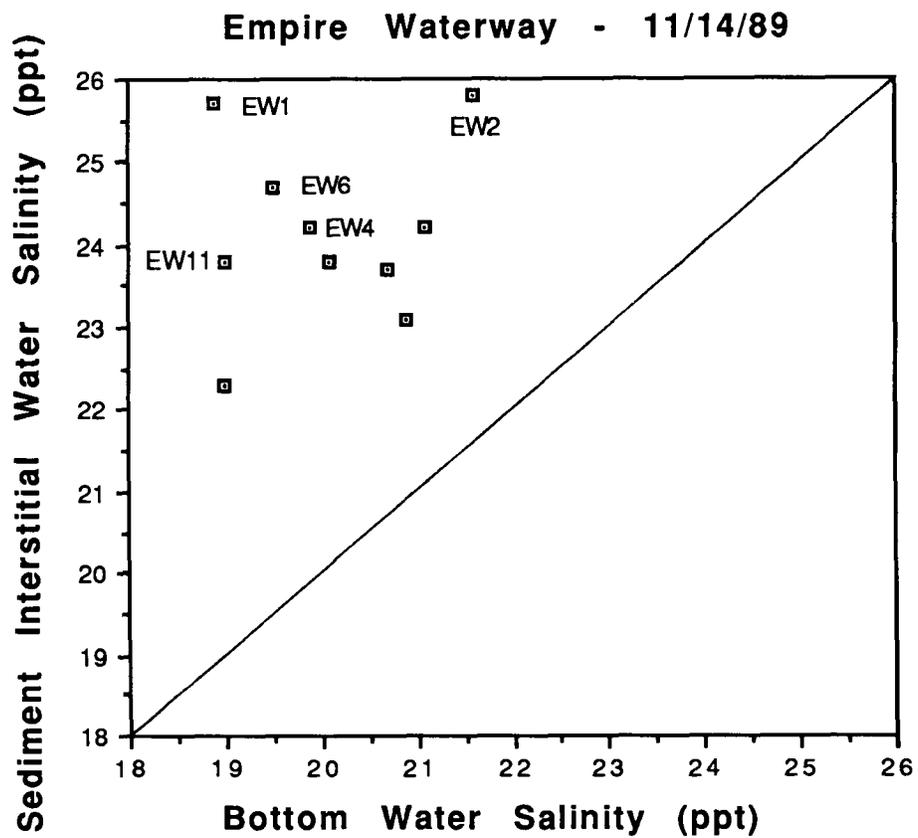


Figure 11.3. Comparisons of interstitial water salinity from surface sediments of stations in the Empire Waterway study area and near-bottom water salinity. Station number given for values most different from a 1:1 relationship (indicated by diagonal line).

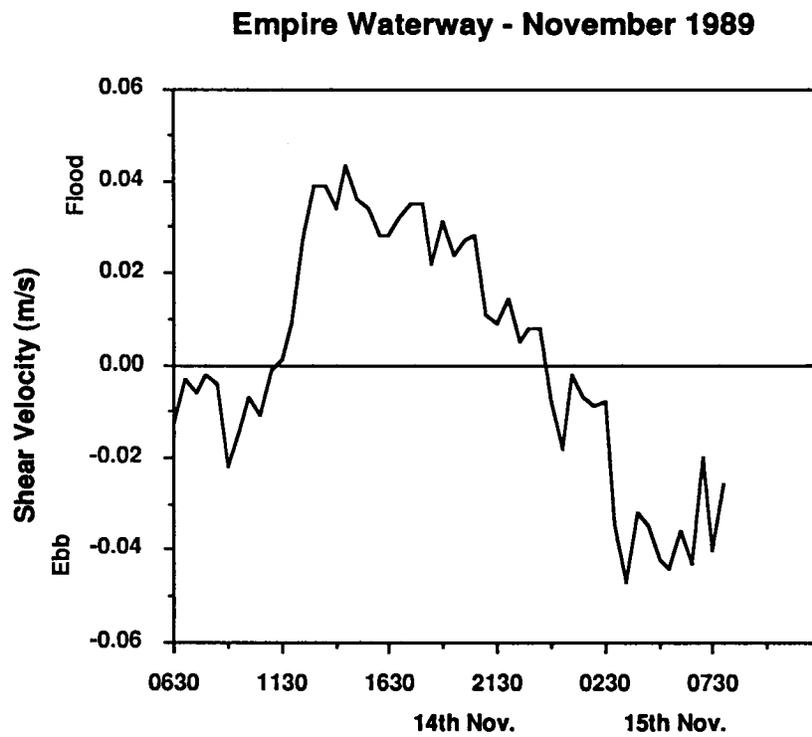
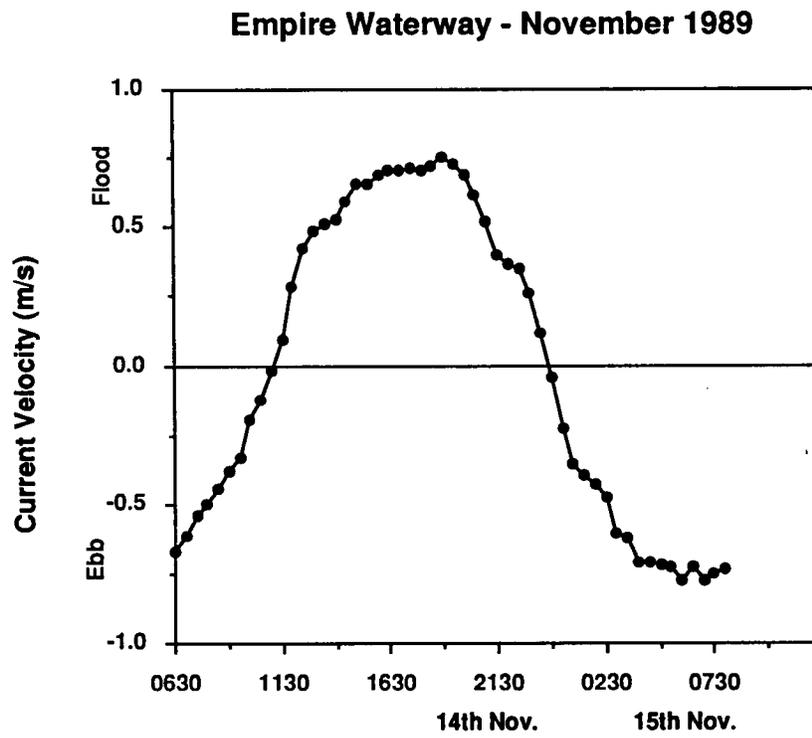


Figure 11.4. Mean tidal current velocity variation and calculated shear velocities for Empire Waterway, November 1989.

EMPIRE WATERWAY: NOVEMBER 1989

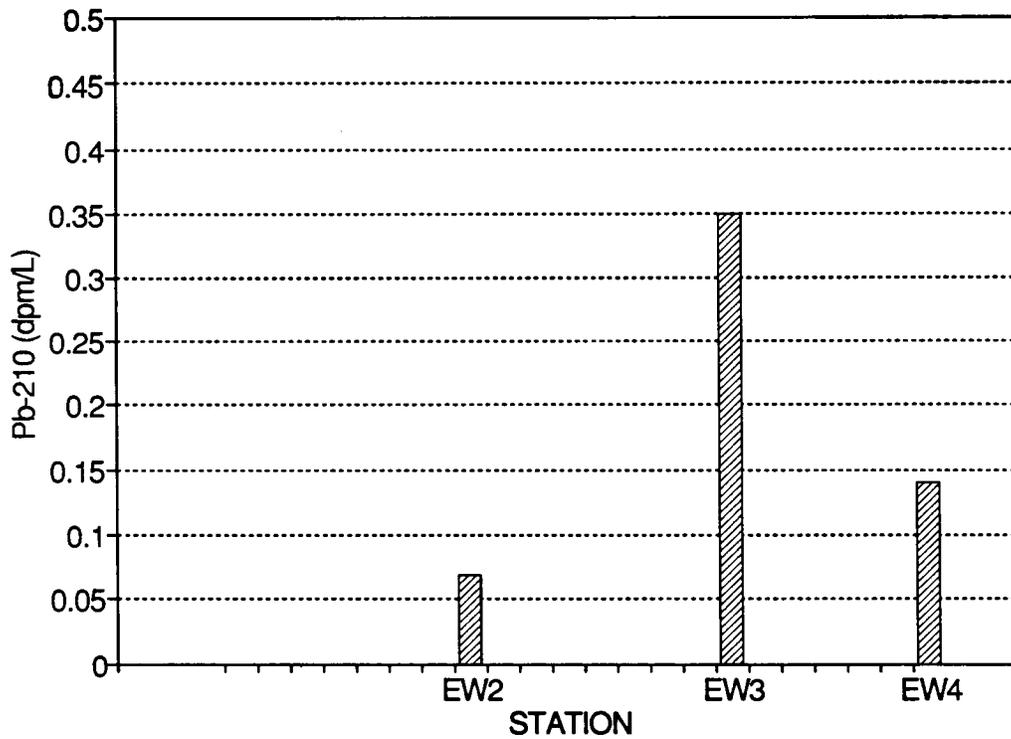
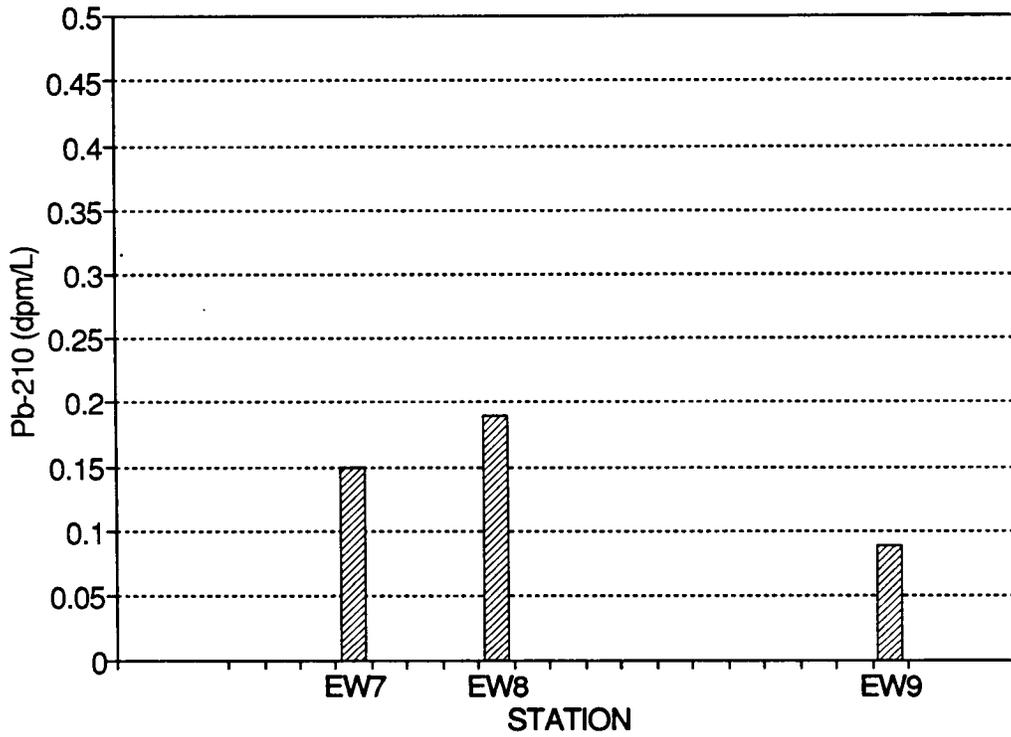


Figure 11.5. Spatial distribution of Pb-210 activities in Empire Waterway near-bottom waters, November 1989.

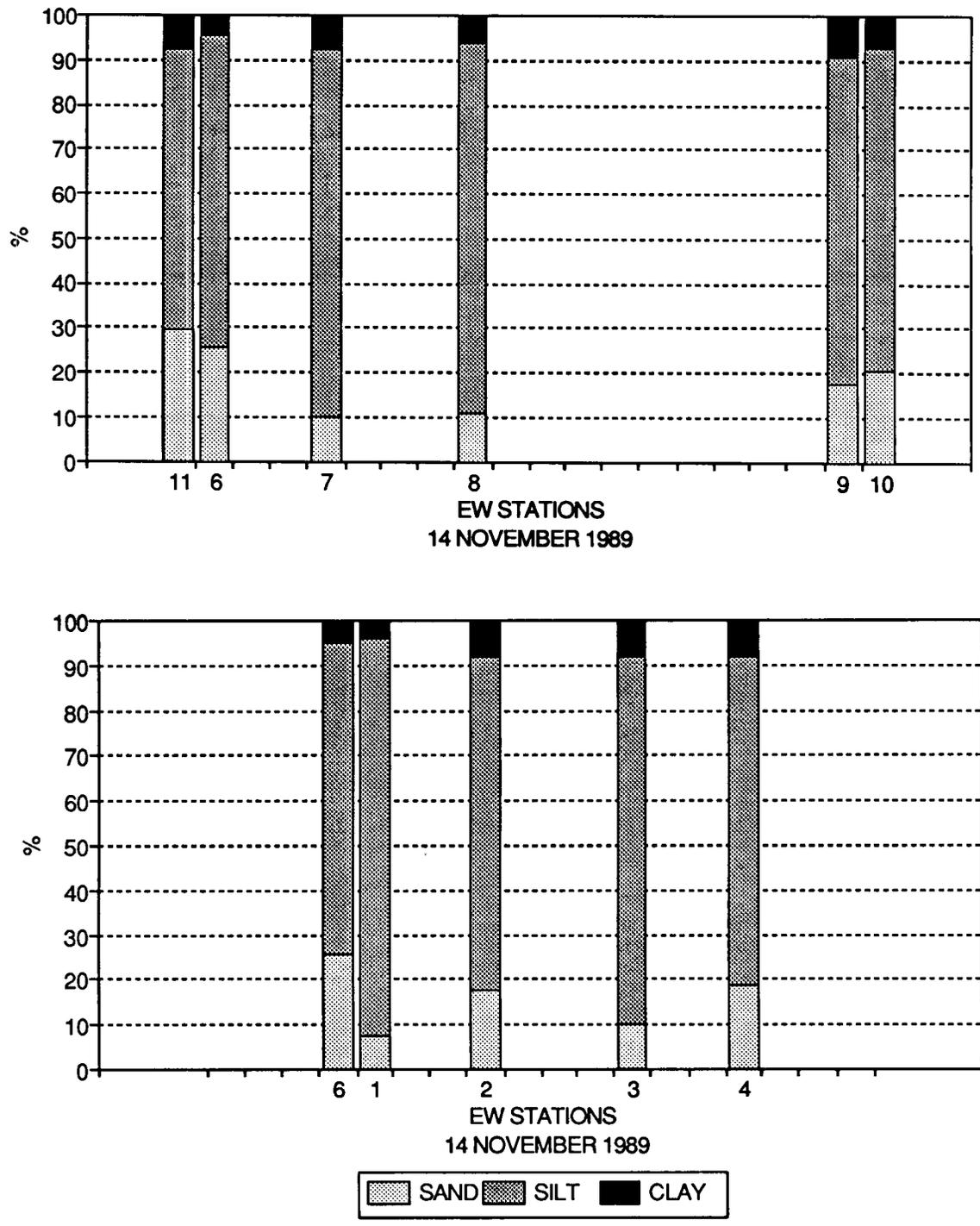


Figure 11.6. Spatial distribution of surface sediment grain size from Empire Waterway, November 1989.

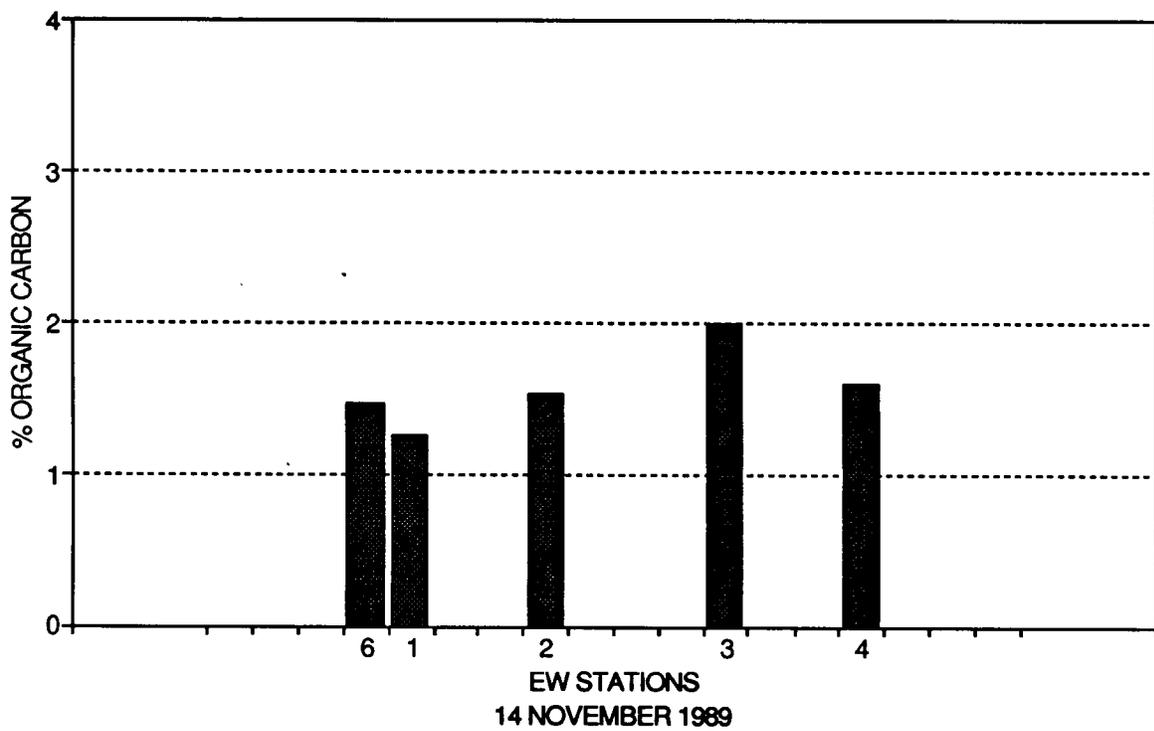
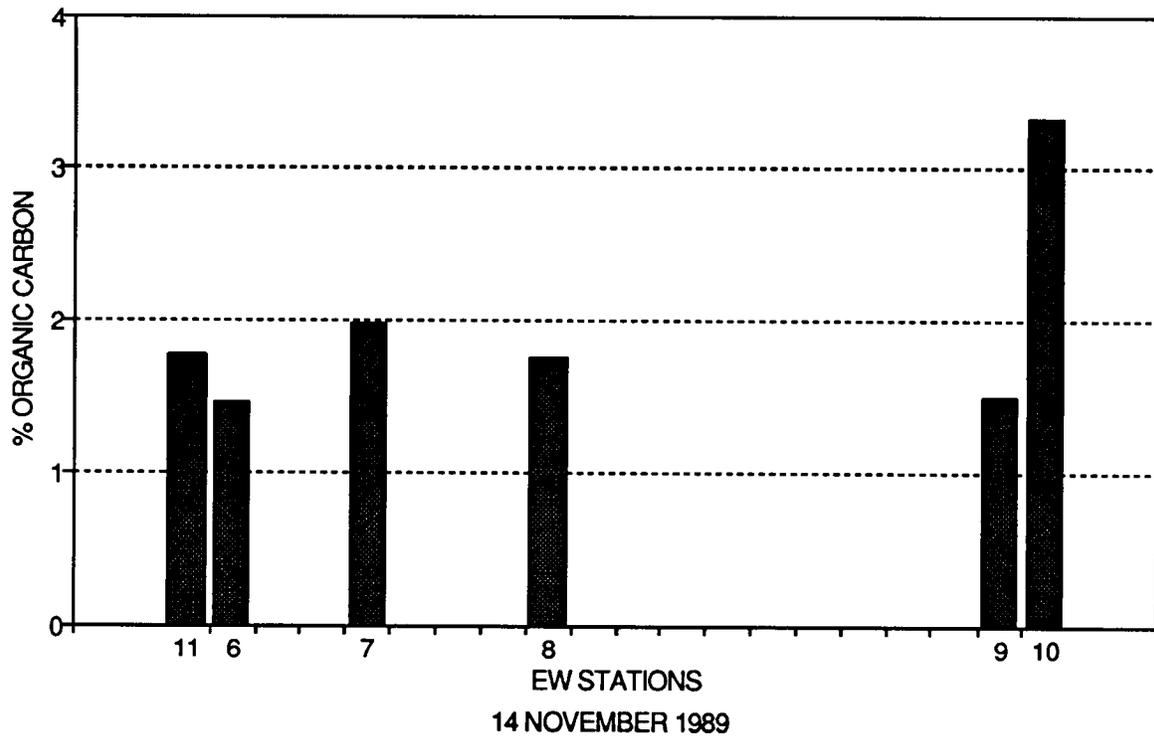


Figure 11.7. Spatial distribution of percent total organic carbon in surface sediments from Empire Waterway, November 1989.

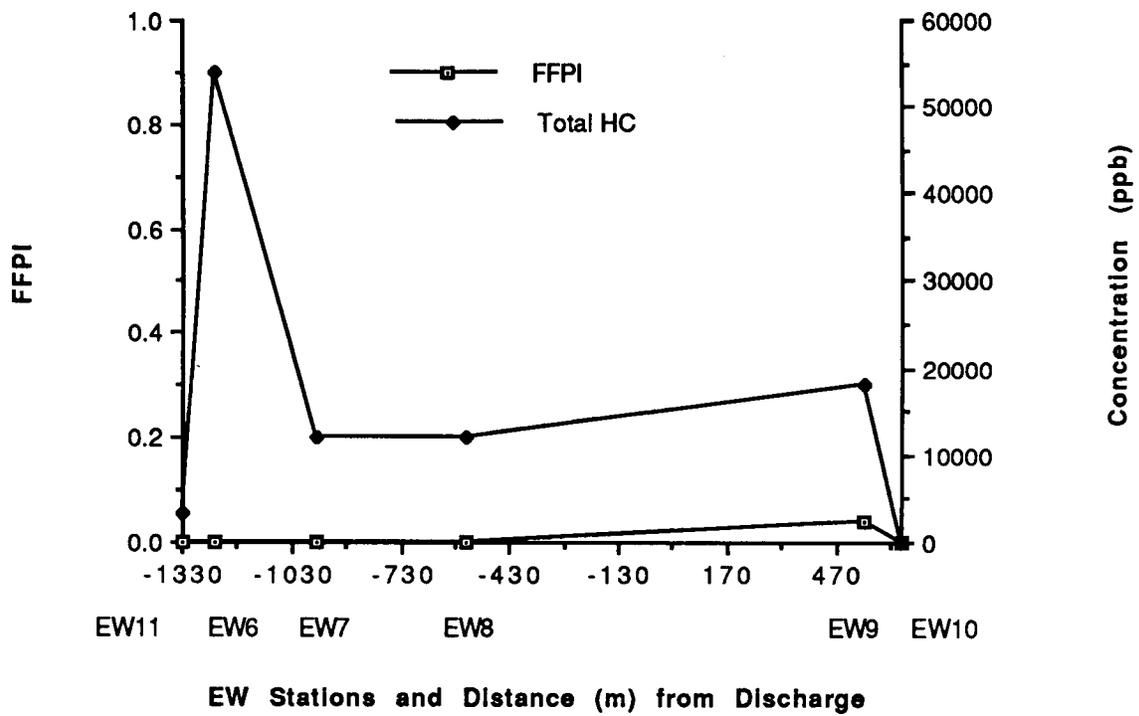
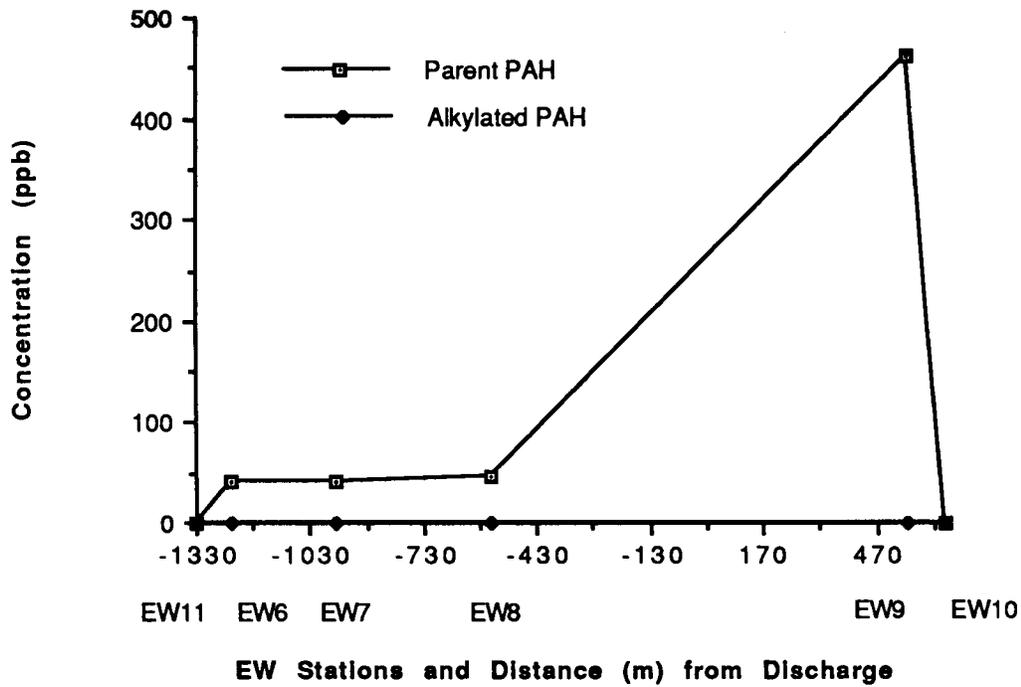


Figure 11.8. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from stations near the active discharge point in Empire Waterway, November 1989.

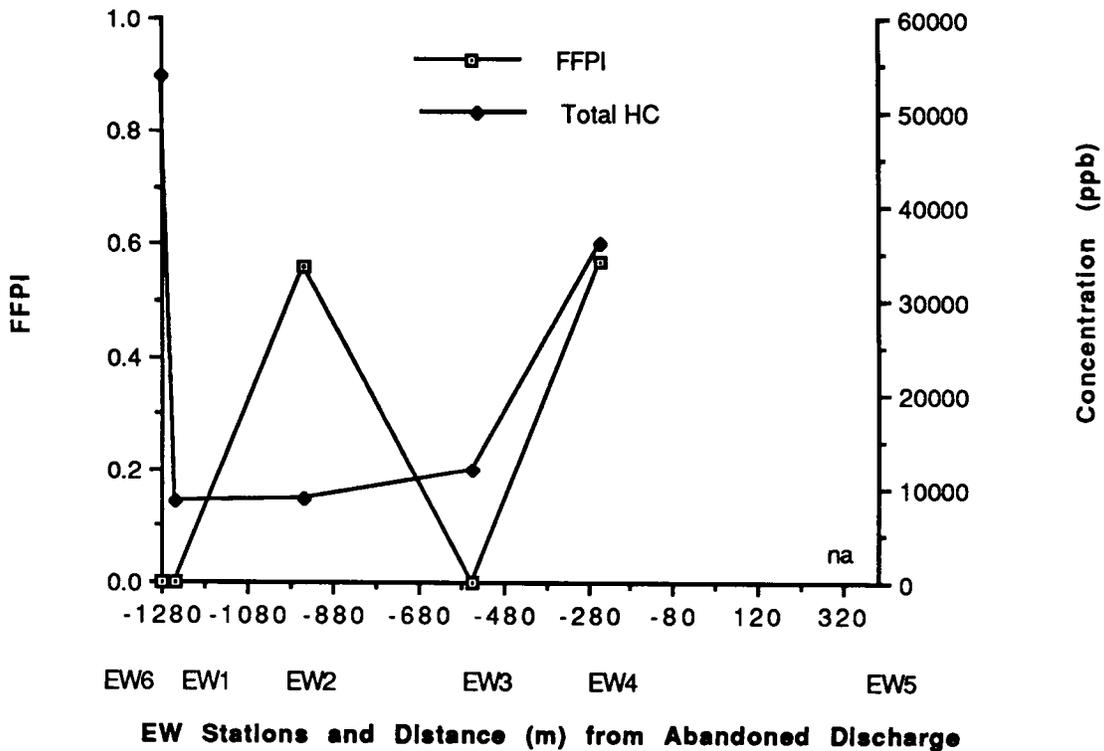
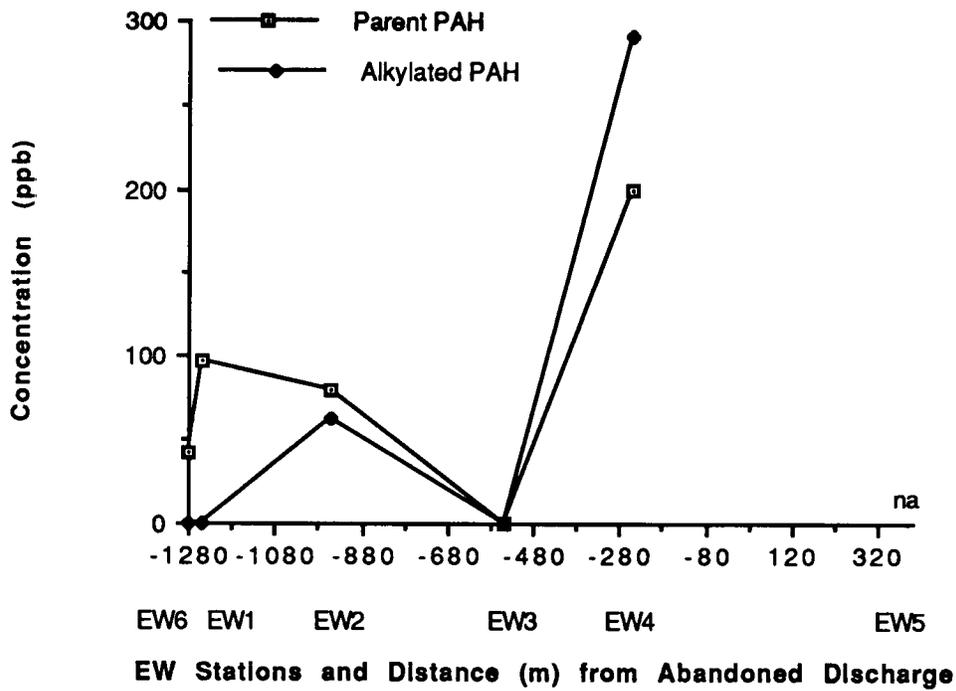


Figure 11.9. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments near the abandoned discharge in Empire Waterway, November 1989.

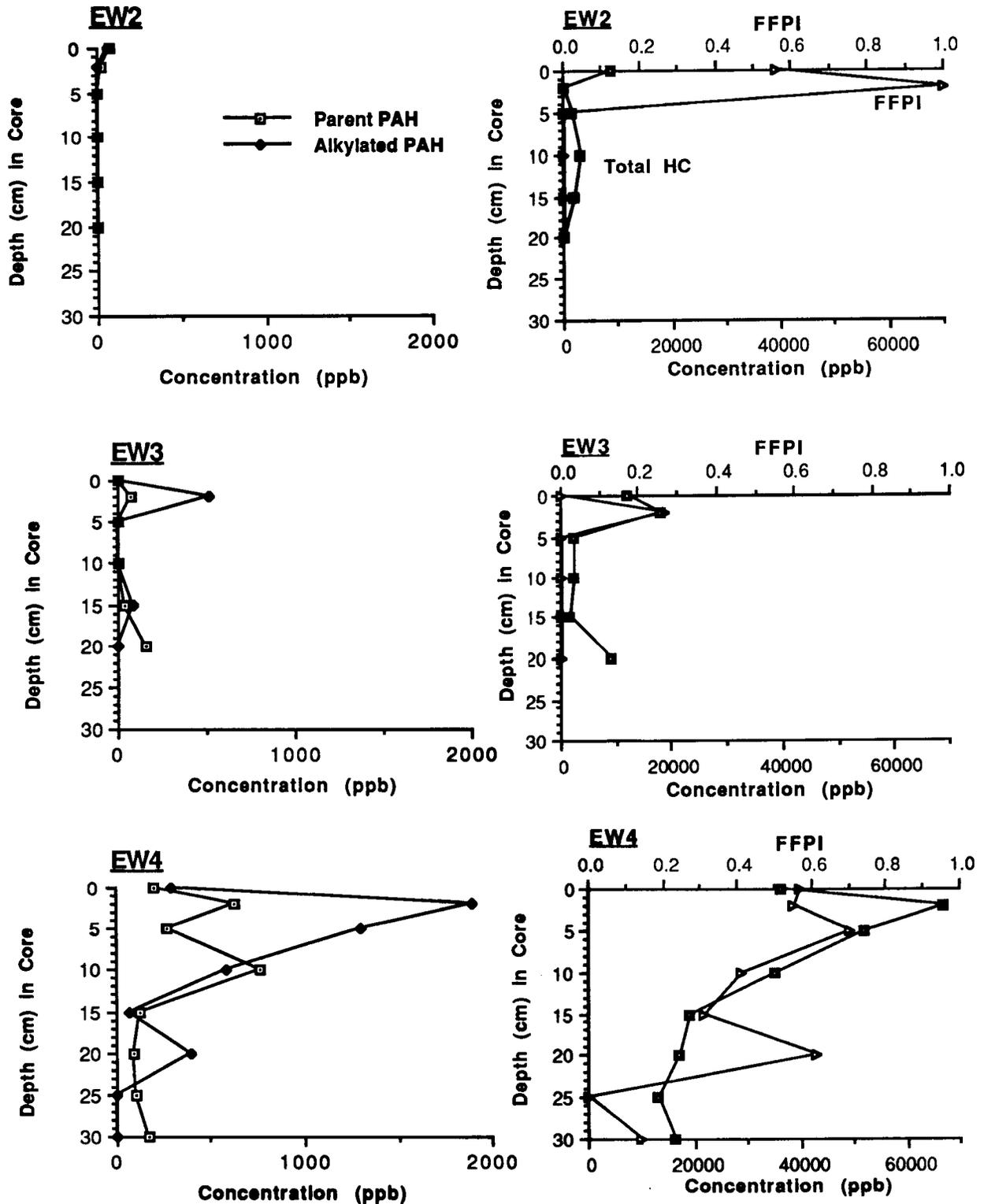


Figure 11.10. Total parent and alkylated PAH concentrations, FFPI and total HC concentrations in vertical sediment core sections from stations near the abandoned discharge in Empire Waterway, November 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

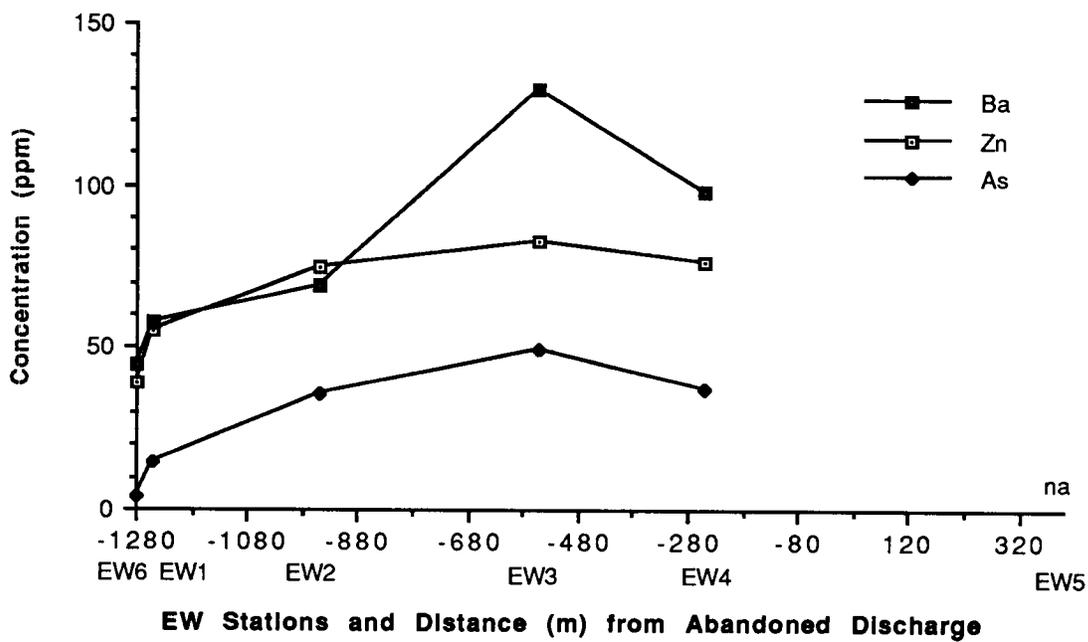
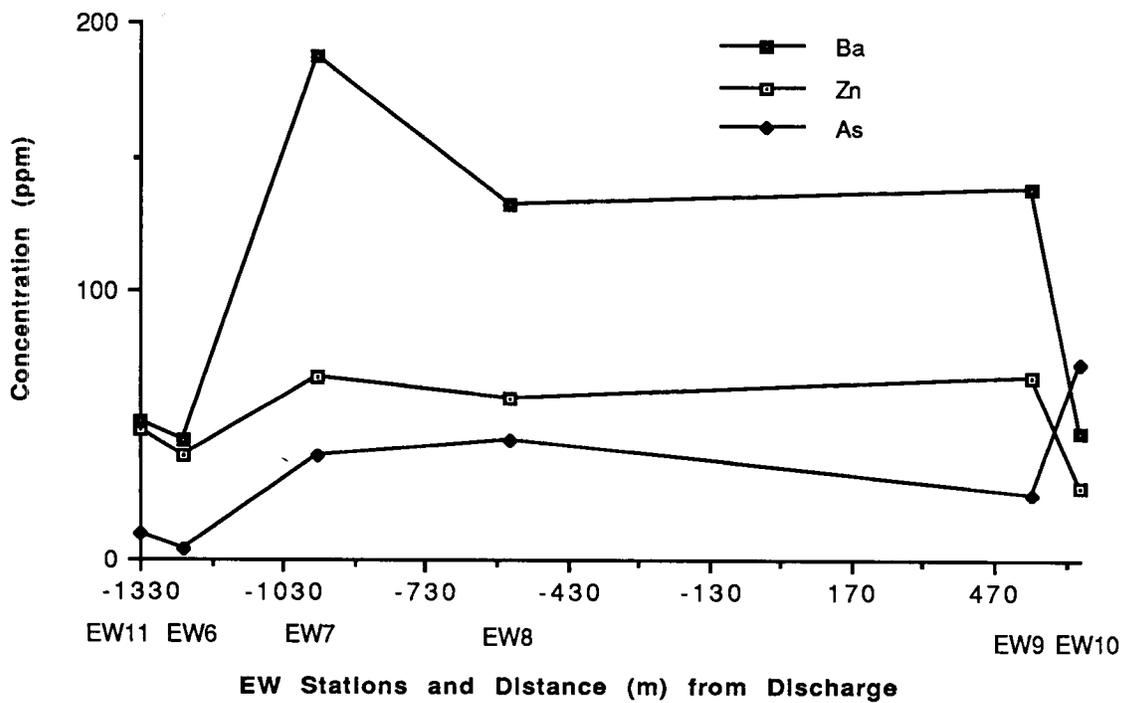


Figure 11.11. Spatial distribution of selected trace metal concentrations in surface sediments from Empire Waterway, November 1989.

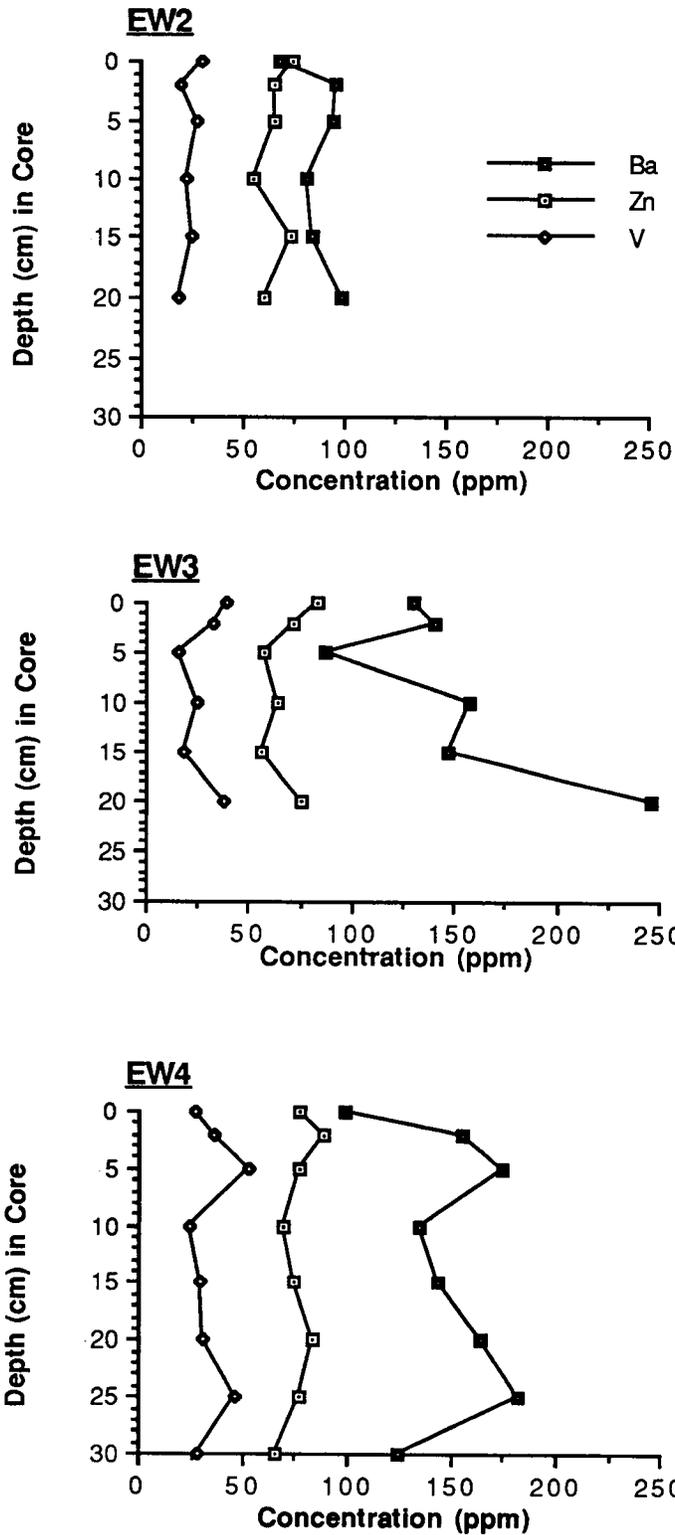
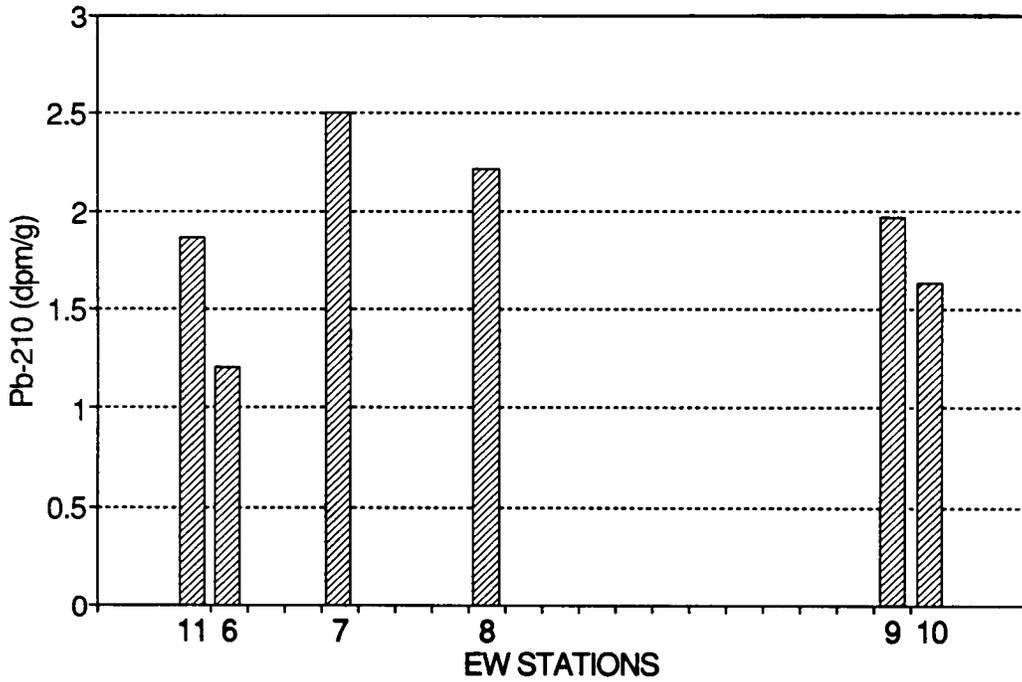


Figure 11.12. Selected trace metal concentrations in vertical sediment core sections from stations near the abandoned discharge in Empire Waterway, November 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.)

EMPIRE WATERWAY: NOVEMBER 1989
SURFACE SEDIMENT Pb-210



EMPIRE WATERWAY: NOVEMBER 1989
SURFACE SEDIMENT Pb-210

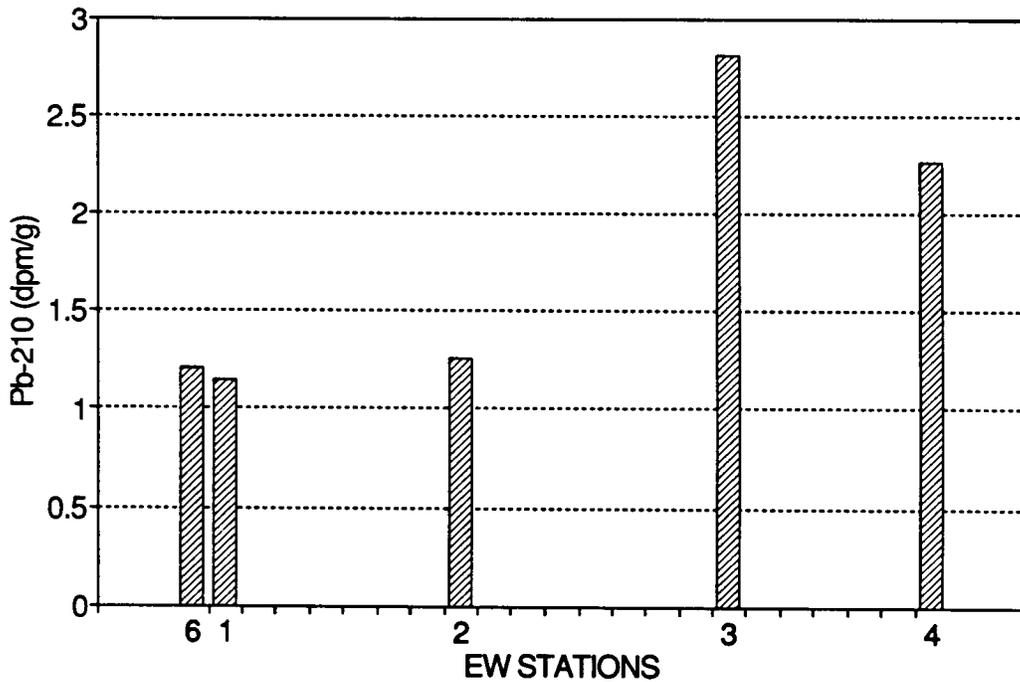


Figure 11.13. Spatial distribution of Pb-210 activities in surface sediments from Empire Waterway, November 1989.

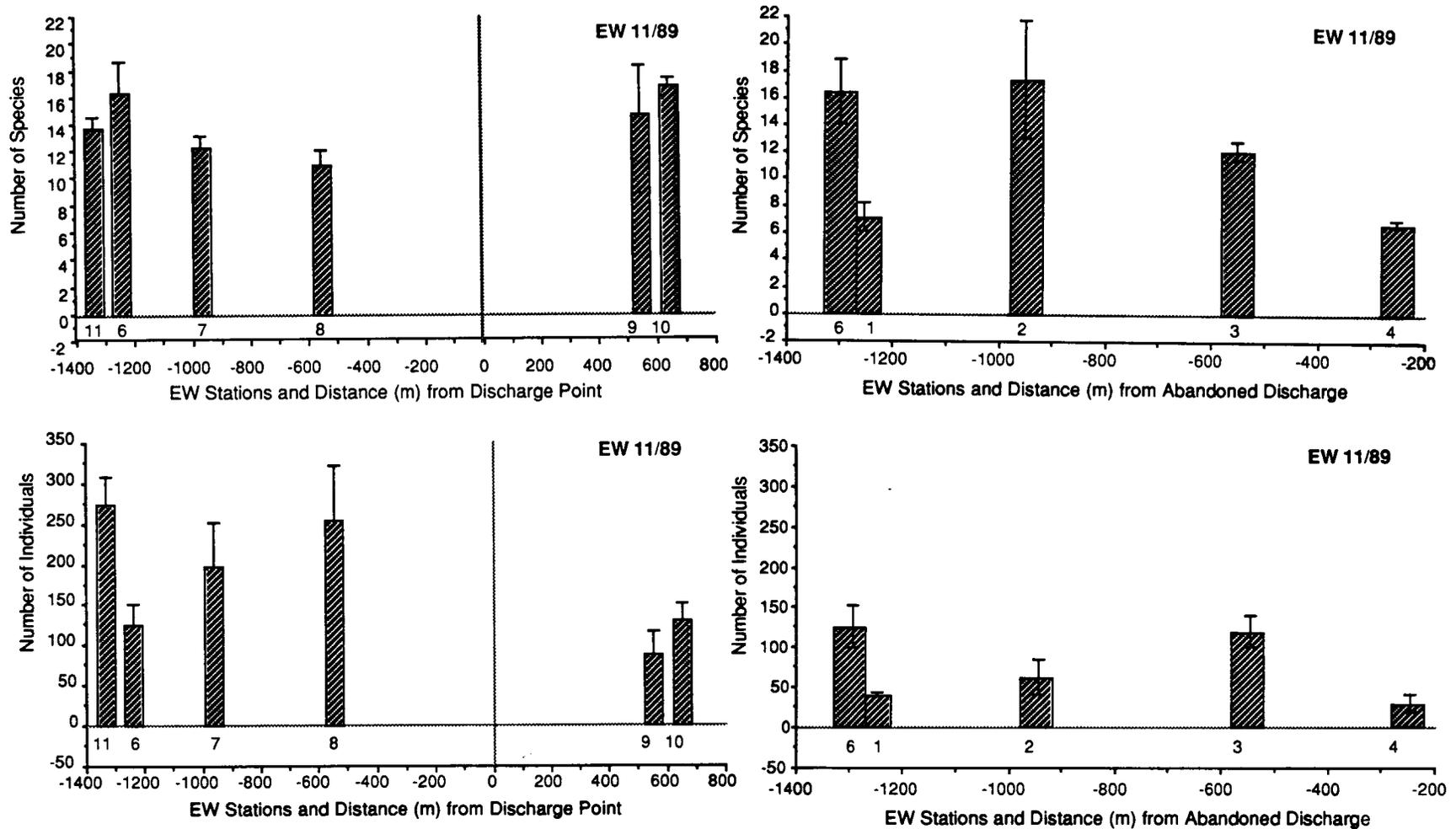


Figure 11.14. Spatial distribution of number of species per replicate (mean \pm standard error) and number of individuals per replicate (mean \pm standard error) for Empire Waterway, November 1989.

Table 11.1. Comparison of average daily discharges ($\text{bbl}\cdot\text{d}^{-1}$) and oil and grease content ($\text{mg}\cdot\text{l}^{-1}$) of produced waters from facilities at Empire Waterway study area. Volumes in <brackets> are discontinued. (Data provided by operators.)

Date	Facility	
	West Delta 30 Terminal	Pelican Island Terminal
11/89		
Discharge	10,742	----
Oil and Grease	42	----
Average Discharge	10,959**	<12,000 - 15,000>
Average Oil and Grease	26*	
Discharge Estimated in Boesch and Rabalais (1989a)	2,000	15,000
Discharge as of 03/91	15,000	----

* Mean of 25 monthly sample dates from 02/88 - 02/90.

** Mean of 4 monthly sample dates from 02/89 through 02/90.

Table 11.2. Duncan's multiple range test for Empire Waterway study area, stations near discharge point; underlined stations are not significantly different from each other.

Number of Individuals (natural log transformed):

EW11 EW8 EW7 EW10 EW6 EW9

Diversity (H') (natural log transformed):

EW6 EW9 EW7 EW10 EW8 EW11

Evenness (J')

EW6 EW9 EW7 EW8 EW11 EW10

Table 11.3. Duncan's multiple range test for Empire Waterway study area, stations near abandoned discharge; underlined stations are not significantly different from each other.

Number of Species:

EW2 EW6 EW3 EW1 EW4

Number of Individuals (natural log transformed):

EW6 EW3 EW2 EW1 EW4

Diversity (H'):

EW2 EW6 EW3 EW4 EW1

Chapter 12

BIOACCUMULATION

12.1 Introduction

A key aspect of a complete ecological and human risk assessment for produced water discharges must address the bioavailability and bioaccumulation potential of the contaminants found in these discharges. One approach which has been used in many such assessments has been the collection and analysis of indigenous populations of non-migratory species in the area of a discharge site and in a spatial gradient away from that site. Bivalve molluscs such as the oyster (*Crassostrea virginica*) or the blue mussel (*Mytilus edulis*) have been used successfully in several large-scale biomonitoring studies in estuaries and coastal marine environments (Farrington et al. 1983, Neff et al. 1976, NOAA 1988). These and other studies have established the scientific validity of such biomonitoring efforts. However, in some situations, the use of indigenous organisms is impractical. For example, in a previous report (Boesch and Rabalais 1989a), we discussed the relative scarcity of natural bivalve populations at or near the produced water discharge sites. This was attributed to the fact that natural populations of these organisms were not available because of modifications to their environment such as dredging, channelization, oil drilling and, potentially, produced water discharges. Therefore, adequate data on the bioavailability and bioaccumulation of produced water associated discharges of toxic metals and organics remains largely incomplete.

In addition to the above stated sampling problems, there remains a certain degree of uncertainty concerning the bioaccumulation of sediment-associated contaminants. Since many of the toxic metals and organics found in produced waters are highly particle reactive and may in some cases be irreversibly sorbed to suspended or bedded sediments, a more detailed examination of the bioaccumulation of these contaminants was proposed. Recently, investigations have been performed by several research groups to establish a predictive relationship between sediment concentrations and bioavailable contaminant levels in organisms living in association with sediments. These experimental studies have suggested that, for a limited number of neutral hydrophobic organic compounds, a toxicant tissue concentration can be estimated (McElroy and Means 1988 and references therein, Foster et al. 1987) from the sediment concentration normalized for organic carbon and the lipid content of the test organism using the following equation:

$$AF = \frac{[\text{toxicant sed. conc./TOC}]}{[\text{toxicant tiss. conc./lipid}]}$$

where, AF is an accumulation factor which is an empirically determined constant equal to ~2.

sed. = sediment
tiss. = tissue
conc. = concentration

If this equation is rearranged and if an AF value is set from literature values, then the maximum expected tissue concentration (on a lipid weight basis) of a compound or series of compounds, such as PAH, can be calculated from sediment data.

To date, no such predictive relationships have been determined for trace metal bioaccumulation from sediments.

12.2 Methods

Oysters obtained from a clean estuarine environment were transplanted into areas adjacent to produced water discharges at Pass Fourchon and at Bayou Rigaud and at a series of stations representing a dilution series away from the discharges. A total of five or six cages were deployed at each station, plus reference stations (Figures 12.1 - 12.3). The oyster cages had to be deployed in shallow areas to avoid interference with boat traffic and to allow somewhat easy recovery and were therefore restricted to a water depth of 1-2 m and a height of ~0.1 m above the sediment. Care was taken at all sites to avoid interference with navigation. An initial deployment in the fall of 1989 at both sites yielded very few survivors due primarily to predation. Therefore, cages were modified in design to exclude predators.

Deployments took place in April and May 1990 and spanned a period of 14 and 27 days, respectively. Previous studies with estuarine and marine bivalves have suggested that this period of time may be insufficient for the organisms to come into steady-state with respect to a static exposure to concentrations of hydrophobic organics (McElroy and Means 1988, Means, unpublished data), however, problems of predation and mortality due to fouling necessitated the use of shorter deployment periods. Following the exposure period, the oysters were recovered and analyzed using the procedures described in the methods section of this report. Special emphasis was placed upon those substances (both metals and organics) found in the discharge water at the specific site. In a few samples radionuclides were also determined, since these elements are also known to bioaccumulate in organisms.

The oyster cages were 28-in x 39-in plastic "bread delivery" trays, which had been conditioned in sea water to leach out any potential interferences (Figure 12.4). Wood was added to the inside of two of the sides for reinforcement, covering holes (protection from predators), and for attachment of netting. Nylon aquaculture netting, 1/8" mesh, (Naltex) was attached with staples to the inside bottom of the case and bricks were attached underneath the case for weight and to keep the cage off the bottom during the exposure period. After putting the oysters in the case, additional nylon netting was affixed to the top of the tray with staples to keep out predators (i.e., stone crabs and oyster drills). A nylon line was tethered to the oyster cage. Once the cage was deployed, the line was played out and attached to a stake hidden on the shoreline to avoid vandalism.

Oysters were obtained the day before deployment from a local seafood supplier. The oysters for the first deployment came from an oyster lease near Casse-tete Island in Timbalier Bay, while the oysters for the second deployment came from West Champagne Bay, which is between Bayou Lafourche and Baratavia Bay. Oysters were removed from the sack and rinsed well with water and kept on ice overnight. Approximately 20% of the oysters were reserved for tagging, weighing and measuring. These oysters were randomly numbered, tags epoxied to the shell, weighed to the nearest gram, and measured (length and width) to the nearest millimeter.

The first deployment consisted of approximately 25 oysters, while only 17 oysters were deployed the second time. For each deployment, five tagged oysters were part of the total oysters deployed. A set of oysters equal in number to that deployed were retained as "control" oysters, which were returned to the laboratory after deployment and maintained frozen until analysis of all oyster samples. The oyster cages were deployed at six sites in Bayou Rigaud and six at Pass Fourchon. These stations corresponded to the sites for which sediment cores and water samples were taken, except in Pass Fourchon where two deployments were made inside Chevron's canal (PF0 and PF200). Two reference sites were chosen in the Pass Fourchon area, far from oil-related activity (Figure 12.2). One was in Bayou Tartellon, PFR1, and the second, in a bayou off the northeast corner of Bay Champagne, PFR2 (Figure 2.2). No reference site was used in Bayou Rigaud because no appropriate area was found. CTD (conductivity/temperature/depth) readings were taken at each area with the average depth of deployment in both areas was

around 1 m (Table 12.1).

Once the deployment period was complete, the cages were retrieved and CTD readings were taken. Live oysters were removed from the trays, placed in labeled Ziploc freezer bags and kept on ice until returned to the lab, where they were frozen at -20°C until analysis. The number of dead oysters was noted and recorded. Tagged oysters were weighed and measured upon return to the field laboratory.

12.3 Results

12.3.1 Mortality and Weight Loss

Table 12.2 lists the number of oysters deployed and percent mortality for both areas and deployment periods. As expected, there was higher mortality during the longer deployment period and at stations closer to the discharge for Pass Fourchon. Generally, the mortality was higher in the Pass Fourchon area than in the Bayou Rigaud area.

Figure 12.5 and Table 12.3 show the percent weight change for oysters during both deployments. During the first deployment, oysters at stations PF0, PF200, PF400 and BR11 displayed lower weight gain than the oysters at the reference stations. The lower weight gain for the oysters from Pass Fourchon was probably the result of the produced water discharges. With station BR11, this was not the case. The low weight gain may have resulted from stress induced during the deployment from potential burial of the tray with silts. Oysters from stations PF0 and PF200 again showed lower weight gains during the second deployment than oysters deployed at all other stations.

12.3.2 Hydrocarbons

12.3.2.1 Pass Fourchon

Oysters transplanted to the Pass Fourchon study area were found to accumulate high tissue concentrations of both alkylated PAH and total HC associated with the produced water discharges. Figure 12.6 (Table H.1) shows the accumulated residues of alkylated PAH, total PAH, total HC and values of FFPI calculated for the aromatic fraction detected in the oyster tissues on a lipid weight basis from the first deployment. First, it should be noted that both alkylated PAH and total PAH were very low both in the controls (randomly selected oysters from the group of organisms just prior to deployment and frozen for analysis) and reference oysters which were deployed at a great distance from any known hydrocarbon sources within the Pass Fourchon region. Duplicate reference samples were nearly identical in all characteristics measured. Significant tissue residues of alkylated PAH were accumulated in the oyster tissues at all stations within 1000 m of the discharge site (PF0). A gradient of decreasing tissue concentrations was observed as a function of distance away from the discharge. Tissue levels in deployed oysters were all greater than reference oysters. FFPI values calculated for the tissue PAH residues indicated that the accumulated PAH had a strong petrogenic signature and that parent PAH were not dominant components of the PAH accumulated. This was also apparent from examination of the total PAH values relative to the alkylated contribution. Alkylated naphthalenes averaged 48% of total PAH, and phenanthrenes averaged 24% over all stations in Pass Fourchon. The composition in oysters from PF1000N showed higher naphthalenes (54%) and lower phenanthrenes (18%) compared to other stations, indicating fresher inputs of petrogenic contaminants compared to adjacent stations. This conclusion was supported by the ratio R/T, which was slightly elevated compared to other stations. Control oysters exhibited an FFPI value of 0.64, suggesting that they contained a mixture of both pyrogenic and petrogenic PAH at low levels before deployment.

Total hydrocarbon concentrations in control and reference site oysters were nearly identical and relatively low (<700 ppm). At PF0, the transplanted oysters accumulated ~3,000 ppm of total hydrocarbons during the first deployment. A decline in tissue hydrocarbon concentrations was observed as a function of distance away from the discharge. At 600 and 800 m away from the discharge, the tissue hydrocarbon levels were near background (reference) levels. A slight increase observed at PF1000 may be attributable to the ship traffic in the area with the commensurate releases of fuel hydrocarbons.

A second deployment of oysters at the Pass Fourchon site yielded results which were similar to those described for the first deployment (Figure 12.7, Table H.2); however, the levels of both alkylated PAH accumulated and total hydrocarbons accumulated were approximately one-half of those measured after the first deployment. The tissue residues were dominated by produced water-associated alkylated PAH as reflected both in tissue concentrations of these compounds and also in the FFPI values calculated for the tissues PAH residues. The relative composition of alkylated PAH was similar to that observed in the first deployment, with naphthalenes ranging from 52% of total PAH at PF0 and decreasing slightly to an average of 46% in stations beyond 400 m. The only other difference observed was that the maximum alkylated PAH residues were observed in oysters deployed at PF200 rather than at PF0.

It was noted that the oysters deployed for only 14 days accumulated much higher levels of PAH and total HC than those deployed for 27 days. The first deployment occurred early enough in the spring that the oysters had not yet spawned, while the second occurred during the spawning season. It was observed both visually (oyster condition) and analytically (lipid content) that many of the individuals in the cages may have spawned during the second deployment. It has been documented by other investigators that bioaccumulated residues of hydrophobic contaminants such as PAH may be mobilized from the tissues and exported in yolk lipids within the spawned eggs. This may account in part for the lower levels of accumulated PAH residues found in the oysters after the second deployment.

12.3.2.2 Bayou Rigaud

Oysters were deployed along a transect spanning the bayou and extending across both discharges entering the system. Figure 12.8 and Table H.3 show the concentrations of alkylated PAH, total PAH, total hydrocarbons and values of FFPI. All data are presented on a lipid weight basis. Alkylated PAH were accumulated by the oysters at all stations to levels well above control concentrations. No reference site data were obtained for this system due to lack of a suitable habitat; therefore, reference oysters from Pass Fourchon were used for comparisons. The highest levels of alkylated PAH were observed in the oysters deployed nearest to the Conoco discharge point at sites BR2 and BR4. A second maxima was observed at station BR7 which is nearer to the Exxon discharge. FFPI values for all of the accumulated PAH were > 0.9 indicating that petrogenic PAH were the dominant PAH accumulated after deployment. This was also confirmed by the very low actual concentrations of pyrogenic PAH detected in the oyster tissues. Total hydrocarbon concentrations in the oyster tissues followed a similar pattern as a function of distance from the discharges as was observed with alkylated PAH. Tissue concentrations of total HC dropped to near control levels at BR11.

Oysters deployed during the second experiment showed much lower levels of both PAH and total hydrocarbons (Figure 12.9, Table H.4). Alkylated PAH were accumulated at all stations to levels above the controls, however, the maximum concentration observed was approximately half that of the first deployment. The ranking of stations, however, from highest to lowest, was similar to the first deployment with BR4, BR2 and BR7 oysters having highest concentrations. FFPI values and tissue residue data showed that the majority of PAH accumulated during the deployment period were of petrogenic origin.

In the first deployment, relative composition of PAH showed a high average for naphthalenes, 68% of total PAH, while phenanthrenes comprised an average of 11%, with little variation between stations. The second deployment, in contrast, showed an average composition for naphthalenes of 40% of total PAH, and 25% phenanthrenes. Naphthalenes composition was highest at BR4, 60%, and lowest at BR9, 16%, where dibenzothiophenes (25%) were predominant. Aliphatic hydrocarbon concentrations were similar in both spatial distribution and relative concentrations between the stations. As with the PAH the total HC were detected at approximately half of the levels observed during the first deployment. This was attributed to the spawning activity of the oysters during the second deployment and mobilization of tissue lipids.

12.3.3 Trace Metals

The data for 11 trace metals from the first deployment of oysters are listed in Table H.5. Figure 12.10 shows the concentrations of vanadium (V), zinc (Zn), copper (Cu) and barium (Ba) in the oysters deployed in Pass Fourchon and Bayou Rigaud compared to the reference and control oysters. These particular metals have been found to be substantially higher in produced water discharges from south Louisiana (>100 times) than are found in natural waters (Boesch and Rabalais 1989a, Neff et al. 1989, St. Pé 1990, Chapter 4). Oysters deployed in Pass Fourchon and Bayou Rigaud displayed no enrichment in most metals when compared to the reference oysters. The only metal found to be enriched was V in oysters from Bayou Rigaud with a 2-3 fold increase. The accumulation of V may be the result of the produced waters being discharged into Bayou Rigaud, however Ba, which was found in much higher concentrations, was not accumulated by oysters. This suggests that the elevated V concentrations in these oysters may not be from produced waters. V is a relatively volatile metal which is often mobilized into the environment as a result of fuel oil burning. The vanadium found on the oysters in Bayou Rigaud may be from this source. Concentration values for Cu, Pb, Ni and Zn are in the range reported for Louisiana oysters in the NOAA Status and Trends data from 1986 (NOAA 1987). However, Cr and Hg values were about ten times greater than concentrations found in Louisiana oysters (NOAA 1987).

The trace metals data for the second deployment are presented in Figure 12.11 and Table H.6. There was no bioaccumulation by oysters of the majority of metals studied that could be associated with produced water discharges. Aluminum was the only metal that showed any possible correlation between bioaccumulation and proximity to a discharge. Oysters close to the discharges in Pass Fourchon, PF0 and PF200, accumulated high concentrations of aluminum as compared to the reference oysters, where this metal was not detected. High concentrations of aluminum were also detected in oysters deployed in Bayou Rigaud, specifically at BR4 and BR7. The accumulation of aluminum appears to be related to produced water discharges; however, as with the first deployment, Ba, known to be in much higher concentrations in produced water, was not found to be accumulated in these oysters. The lack of correlation between aluminum and barium bioaccumulation again suggests the aluminum concentrations may not be discharge related. The concentrations of Cu, Pb, Cr, Hg and Ni in all types of oyster samples analyzed were substantially higher than those reported in the NOAA Status and Trends 1986 data for any of their study sites throughout the United States.

12.3.4 Radionuclides

Four oyster samples from each deployment (April and May 1990) at the Pass Fourchon study area were examined for levels of radioactivity. Neither control sample contained total radium levels above the detection limit ($0.2 \text{ dpm} \cdot \text{g}^{-1}$). During April 1990, stations PF0, PF200, PF400 and PF1000 were examined for total radium. The sample closest to the discharge point, PF0, had a total radium concentration of $4.3 \text{ dpm} \cdot \text{g}^{-1}$. The next closest station, PF200, had a total radium concentration of $1.1 \text{ dpm} \cdot \text{g}^{-1}$. PF400 and PF1000 had total radium activities below

the detection limit of $0.2 \text{ dpm}\cdot\text{g}^{-1}$. During May 1990, the same stations were re-examined, and only PF0 had a detectable total radium concentration ($2.1 \text{ dpm}\cdot\text{g}^{-1}$).

Three oyster samples from each deployment (April and May 1990) at the Bayou Rigaud study area were examined for levels of radioactivity. Neither control sample contained total radium levels above the detection limit of $0.2 \text{ dpm}\cdot\text{g}^{-1}$. Of the samples examined (BR4, BR7 and BR11), only BR4 during the April deployment had a detectable level of total radium ($1.4 \text{ dpm}\cdot\text{g}^{-1}$).

In a bioaccumulation study near produced water discharges in low-energy, brackish environments of southeastern Louisiana (St. Pé 1990), one of three oyster deployments exhibited an elevated Ra-226 activity ($6.9 \text{ dpm}\cdot\text{g}^{-1}$). This concentration exceeded those found in this study where detectable levels were measured. In this study, total radium activity above the detection limit of $0.2 \text{ dpm}\cdot\text{g}^{-1}$ was measured in four of the 14 samples. These four elevated levels were in oysters deployed adjacent to a discharge (PF0 and BR4), or in one instance 200 m from a discharge (PF200).

12.4 Implications of Bioaccumulated Contaminants

A number of implications may be derived from the transplanted oyster bioaccumulation experiments performed as part of this investigation. First, uncontaminated organisms rapidly (within 14 days or less) accumulate high concentrations of produced water associated contaminants within their tissues. Second, the levels accumulated may exceed the concentrations of contaminants found in ambient sediments in the region. Third, the levels of contaminants found in tissues may be variable with respect to the external exposure environment as the result of seasonal cycles and reproductive activities (e.g., lipid mobilization during spawning).

As suggested in the introduction, laboratory bioaccumulation studies and field investigations have shown that maximum bioaccumulation potential for neutral hydrophobic contaminants such as PAH may be estimated from sediment data. These models suggest that the tissue levels of such contaminants on a lipid weight basis will be related to the sediment levels of the contaminants on a total organic carbon basis by a constant accumulation factor (AF). The values of AF observed in the laboratory and the field range from 0.5 to 2. Some field investigations suggest that for PAH the values may be less than 0.5 due in part to the fact that some of these compounds may be metabolized by the oysters to a limited extent. In these studies values of AF in the range of 0.1 are common. The Environmental Protection Agency has recently incorporated such an estimation approach into their human health risk assessment methodology for shellfish consumption using an AF value of 2 as the worst case estimate (e.g., resulting in the highest maximum estimate of shellfish tissues residues based upon sediment chemical analysis data).

We have taken our data for the April 1990 oyster deployment and compared these tissue data with that for the surficial sediments collected at mid-channel stations during February 1990. Figure 12.12 shows the calculated values of AF derived from these data. In all cases the values of AF determined from the field data are between 0.1 and 2 as predicted. In general, the higher values were found at stations associated with sandy sediments, while the lowest values were found at the most contaminated stations and generally associated with fine-grained sediments. Foster et al. (1987) reported that AF values from sandy sediments were higher relative to those found with fine sediments. The low values ($\text{AF} < 0.3$) have been attributed to a combination of factors including partial metabolism of the PAH, decreased filtration rates in fine sediments and chronic toxicity to the bioaccumulating test organisms. All of these factors may be active at one or more stations in our study. These data suggest that we may be able to employ this model to predict maximum bioaccumulation potential at all other study areas using the sediment data and assuming an average lipid content for a bioaccumulating species. This may be extremely useful in assessing potential environmental impacts of produced water discharges in many areas.

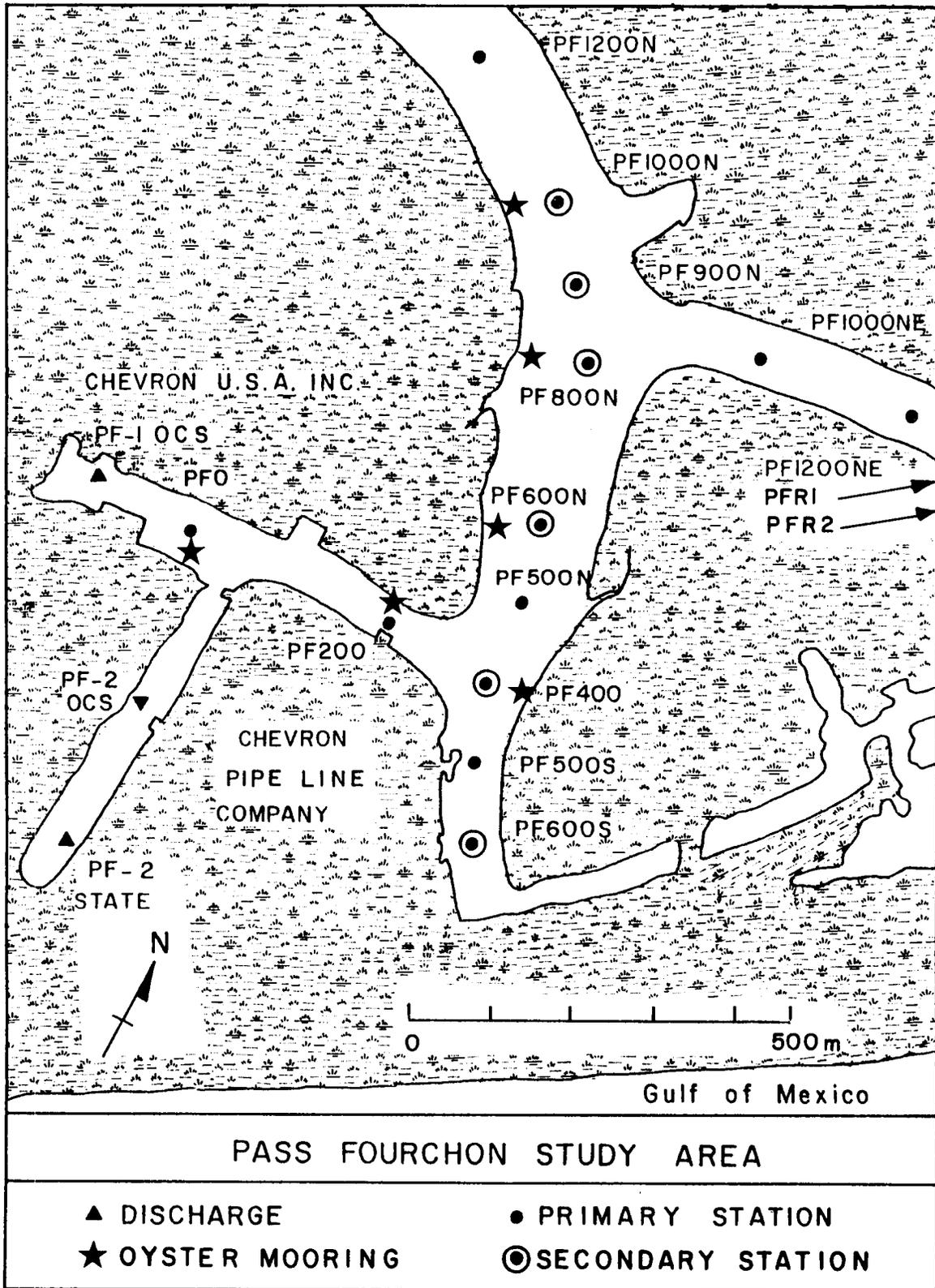


Figure 12.1. Location of stations in Pass Fourchon study area where oysters were deployed. See Figure 12.2 for location of PFR1 and PFR2.

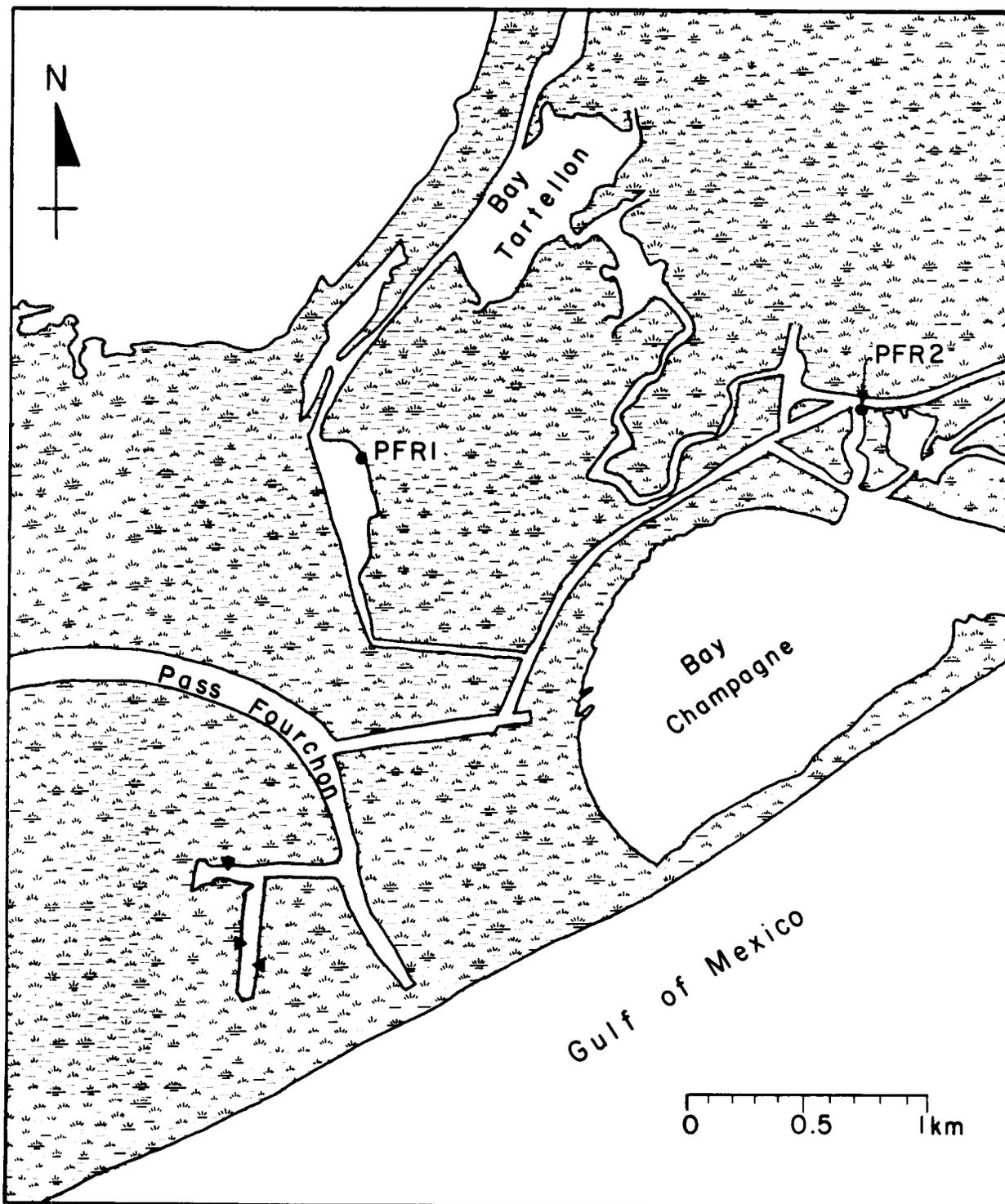


Figure 12.2. Location of reference stations for the oyster deployments at Pass Fourchon and Bayou Rigaud.

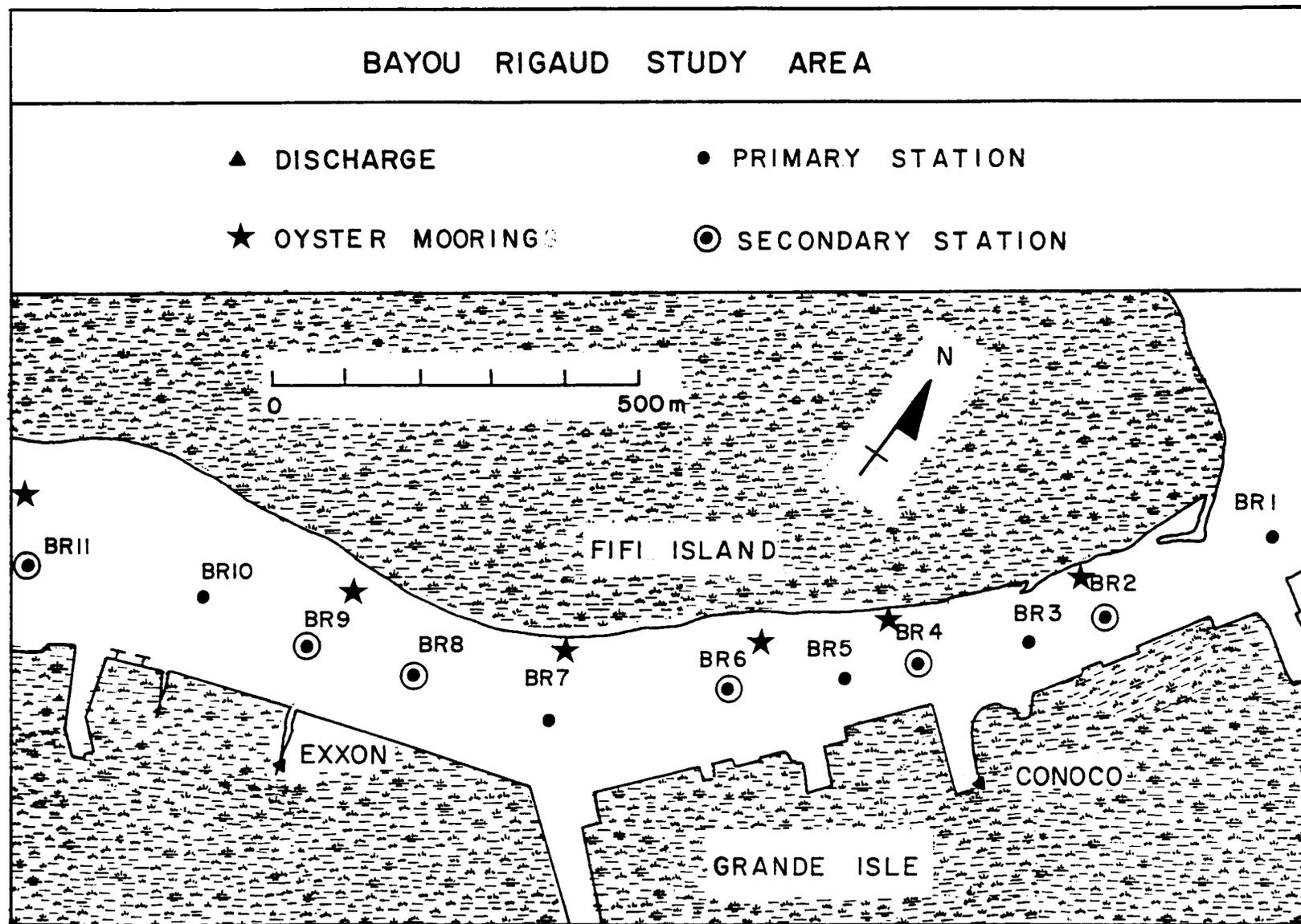


Figure 12.3. Location of stations in Bayou Rigaud study area where oysters were deployed. See Figure 12.2 for location of PFR1 and PFR2.

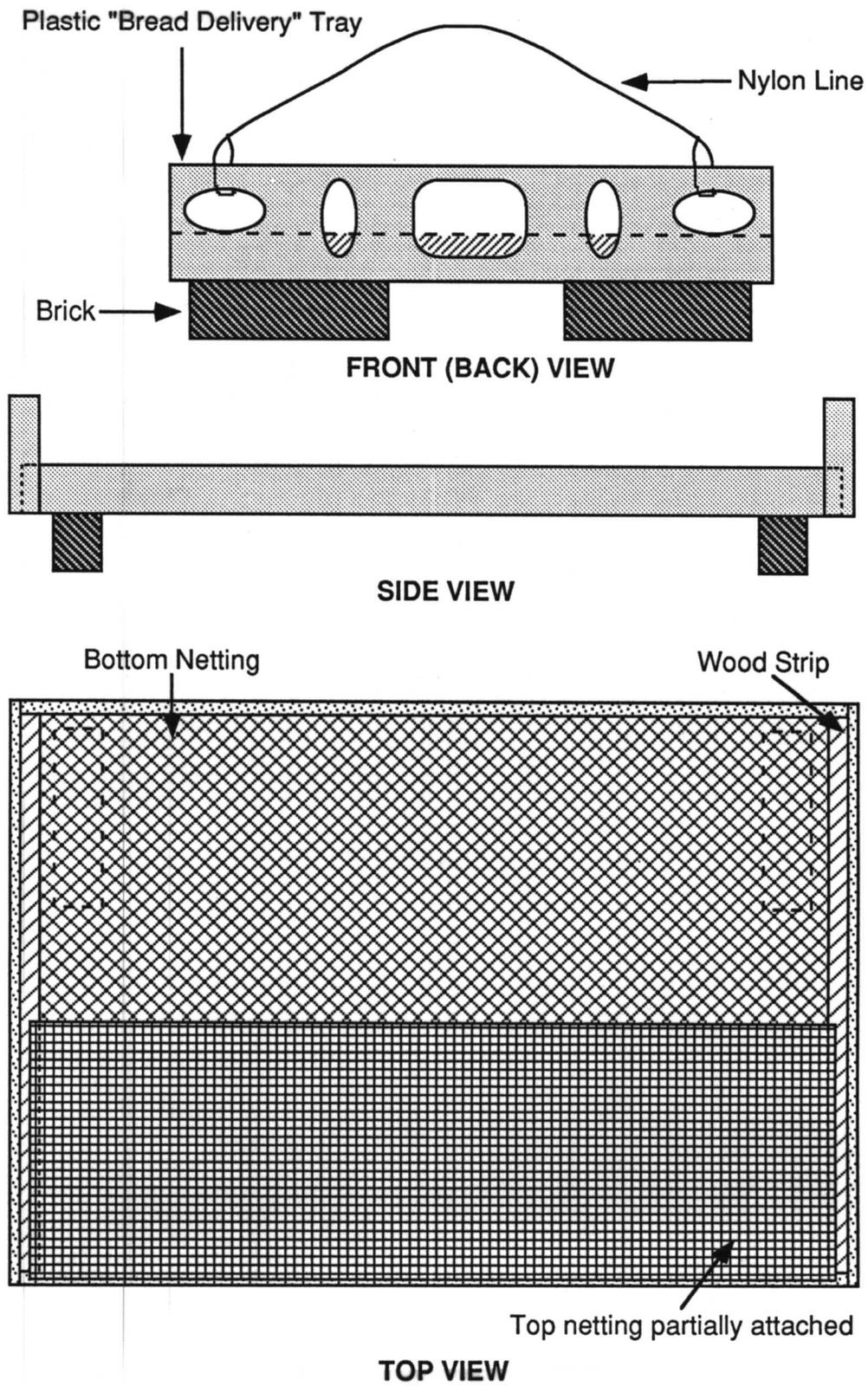


Figure 12.4. Diagram of oyster cages.

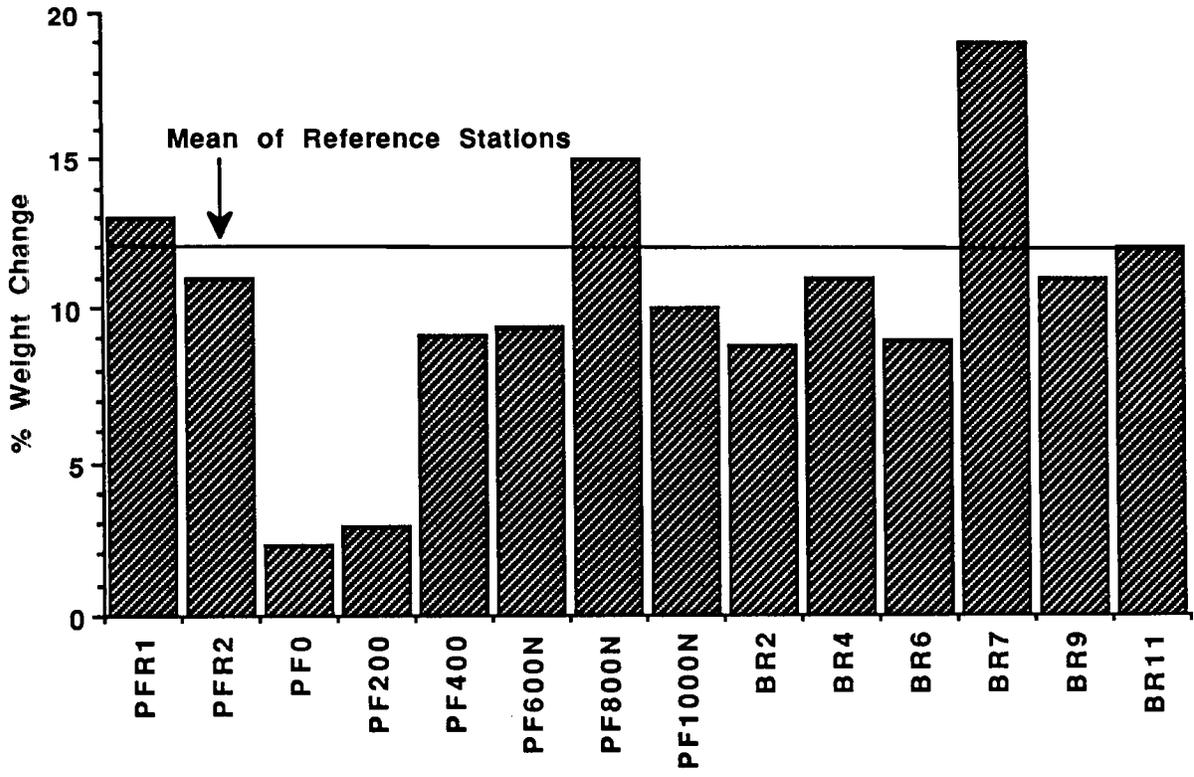
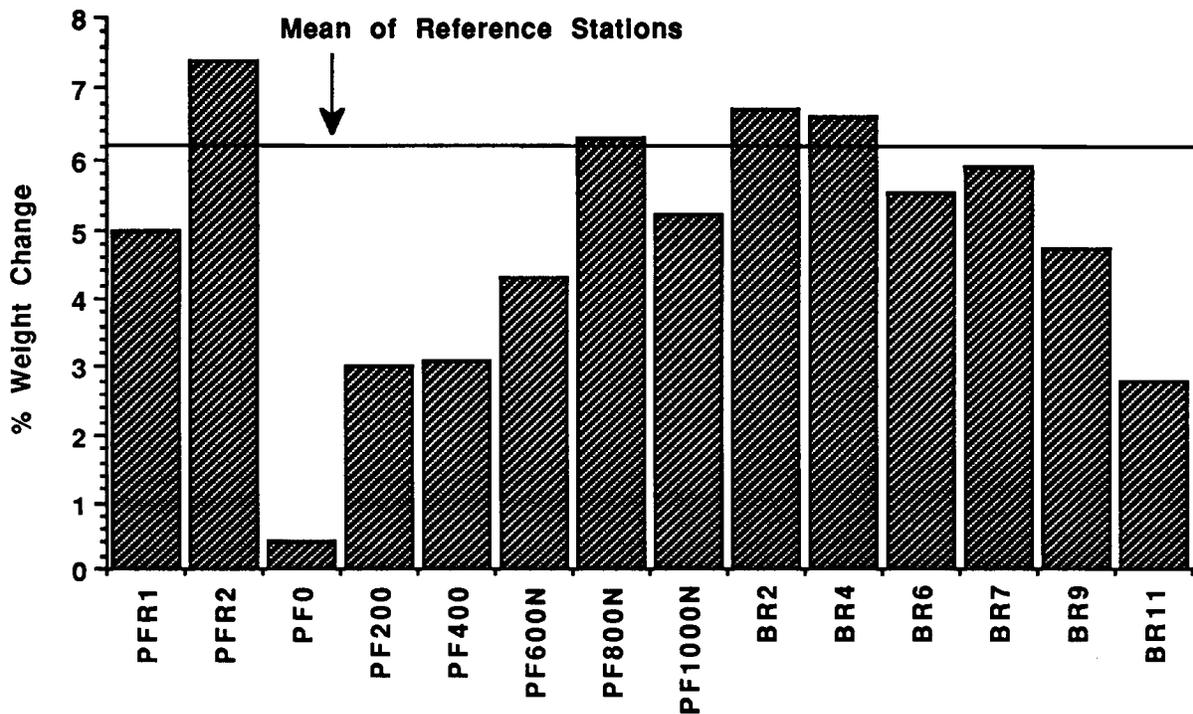


Figure 12.5. Comparison of percent weight change in oysters during the first (top) and second (bottom) deployments. Station locations in Figures 12.1 - 12.3.

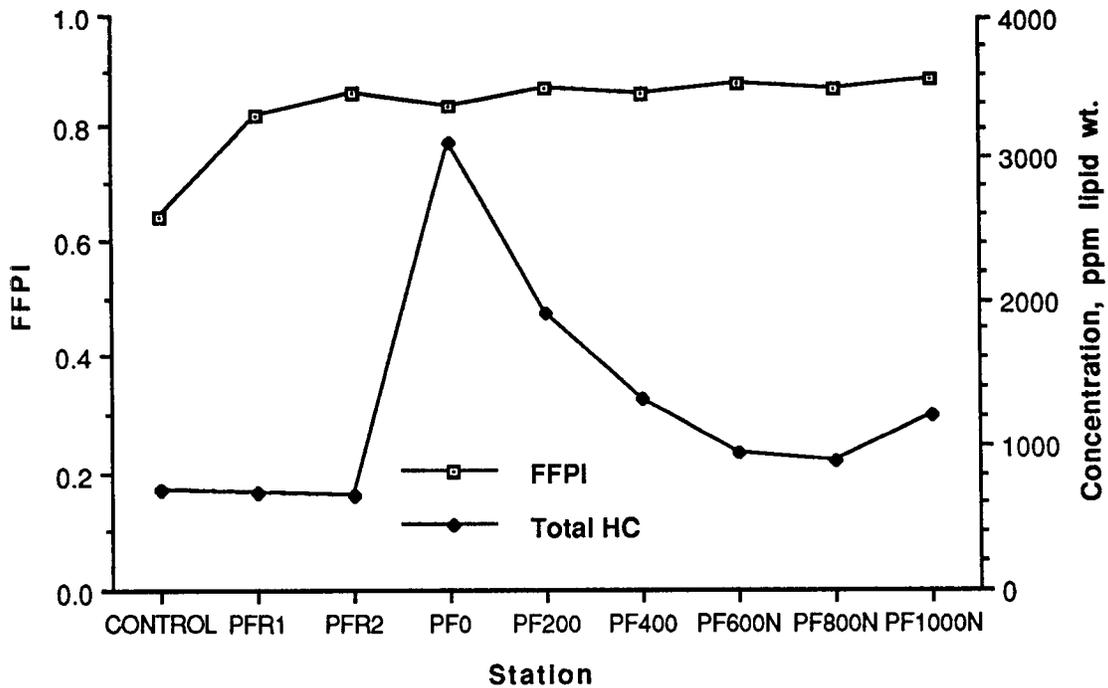
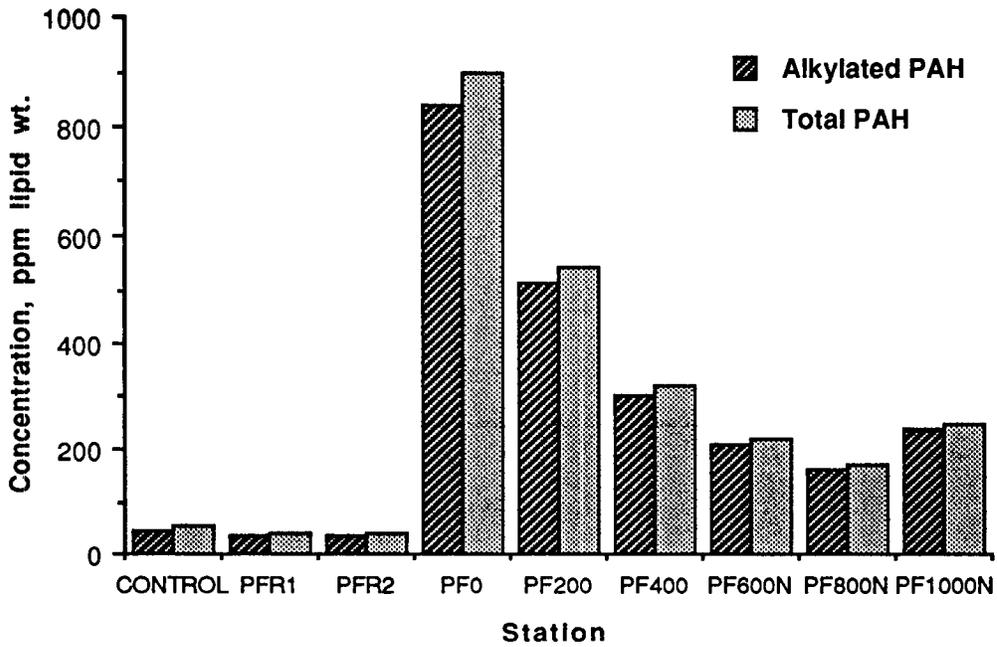


Figure 12.6. Bioaccumulation of PAH and total HC and calculated values of FFPI for oysters deployed in Pass Fourchon for 14 days in April 1990. Station locations in Figures 12.1 - 12.2.

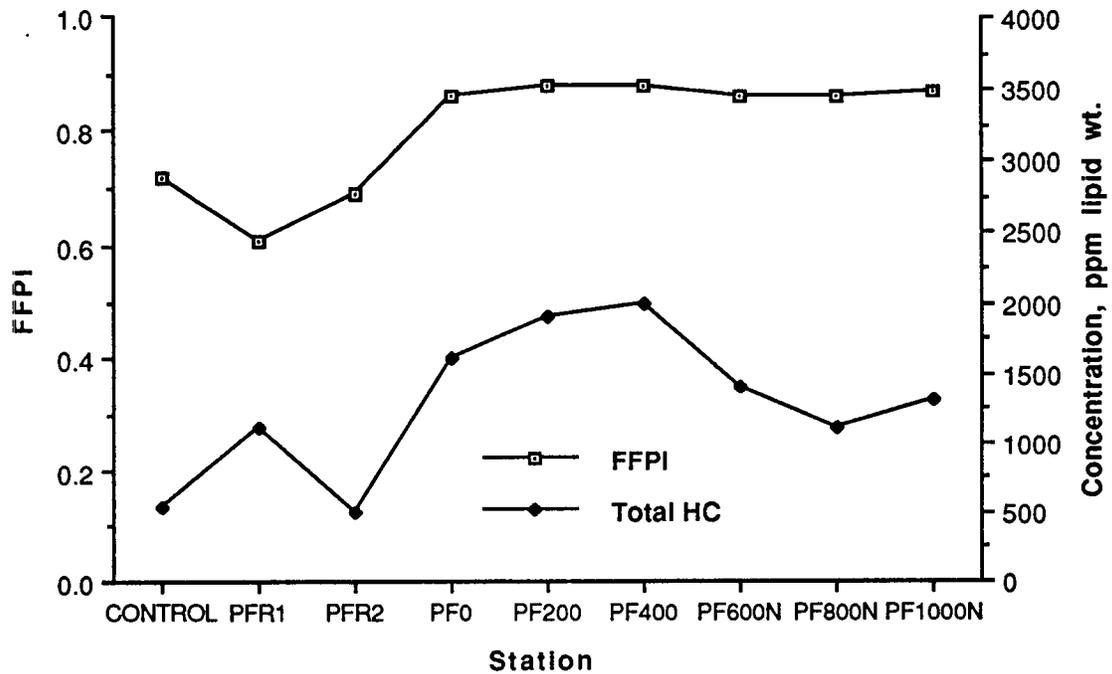
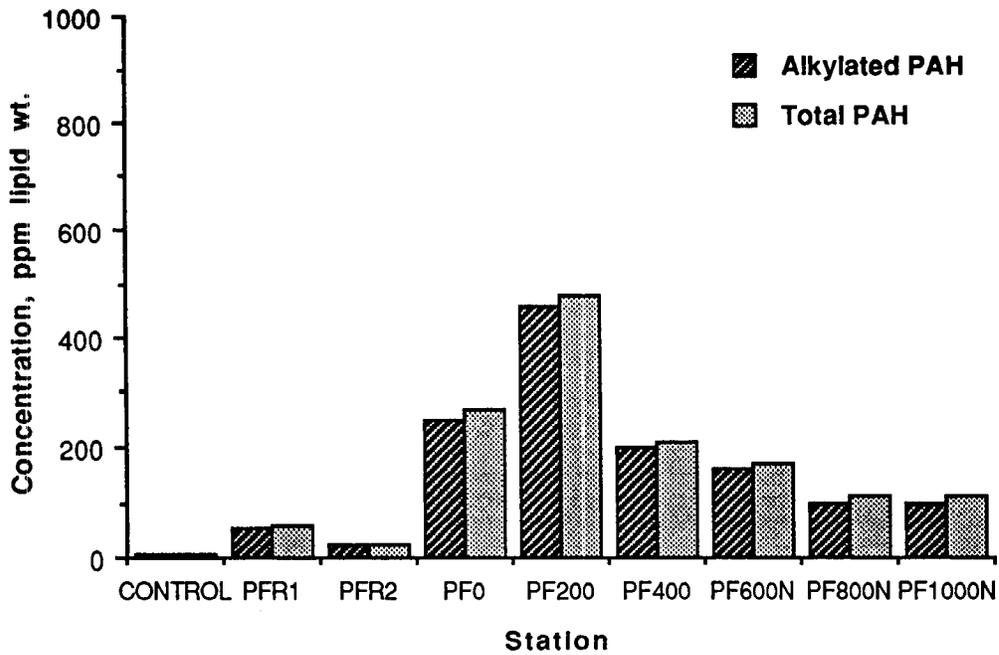


Figure 12.7. Bioaccumulation of PAH and total HC and calculated values of FFPI for oysters deployed in Pass Fourchon for 27 days in May 1990. Station locations in Figures 12.1 - 12.2.

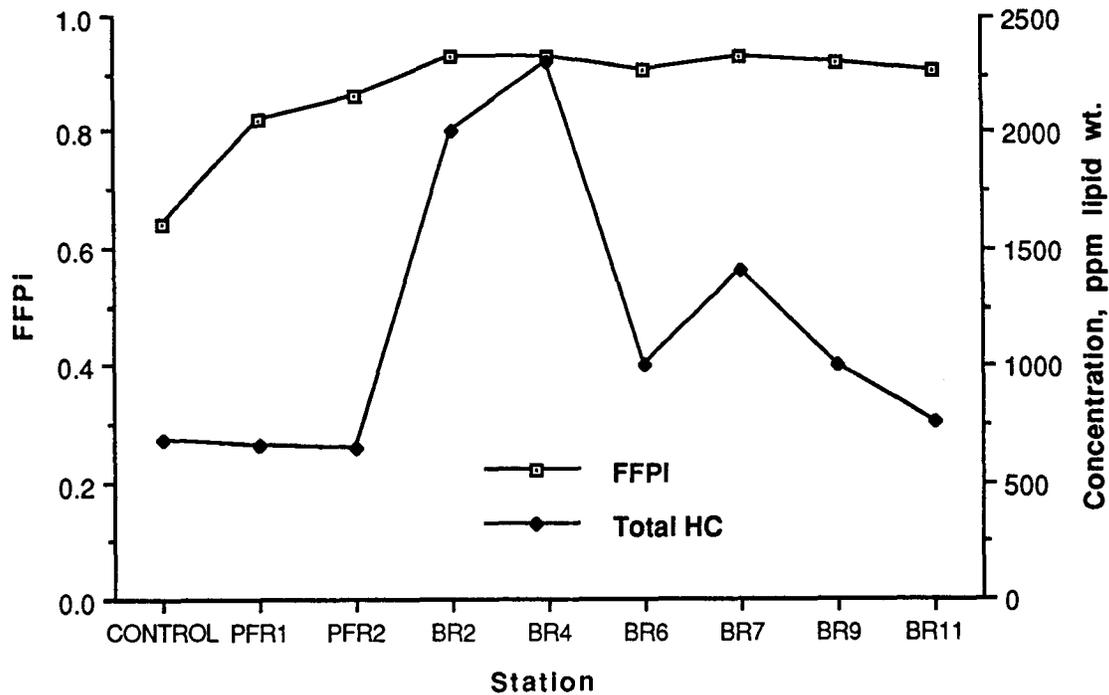
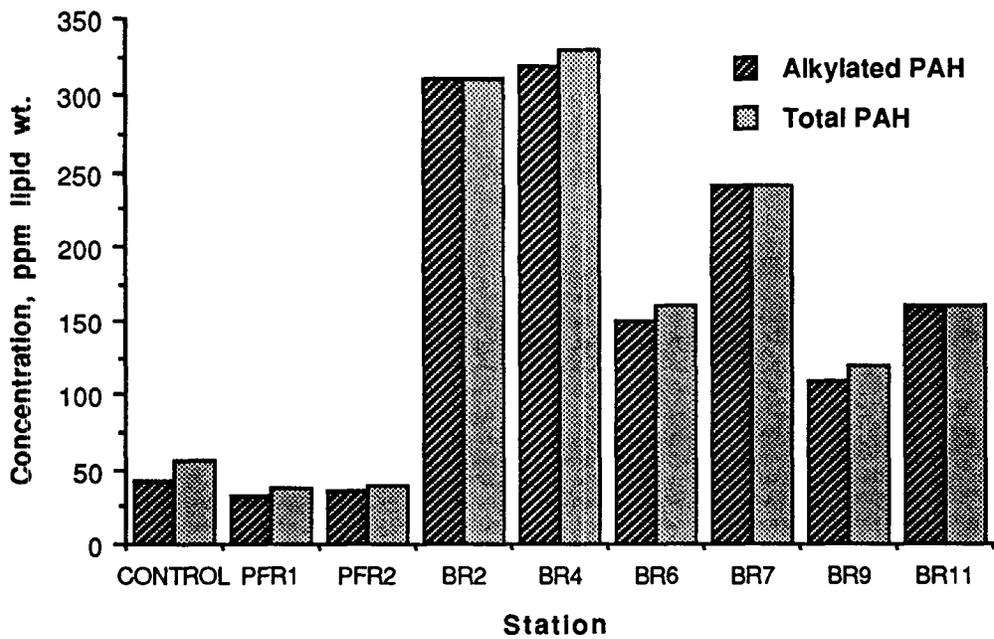


Figure 12.8. Bioaccumulation of PAH and total HC and calculated values of FFPI for oysters deployed in Bayou Rigaud for 14 days in April 1990. Station locations in Figures 12.1 and 12.3.

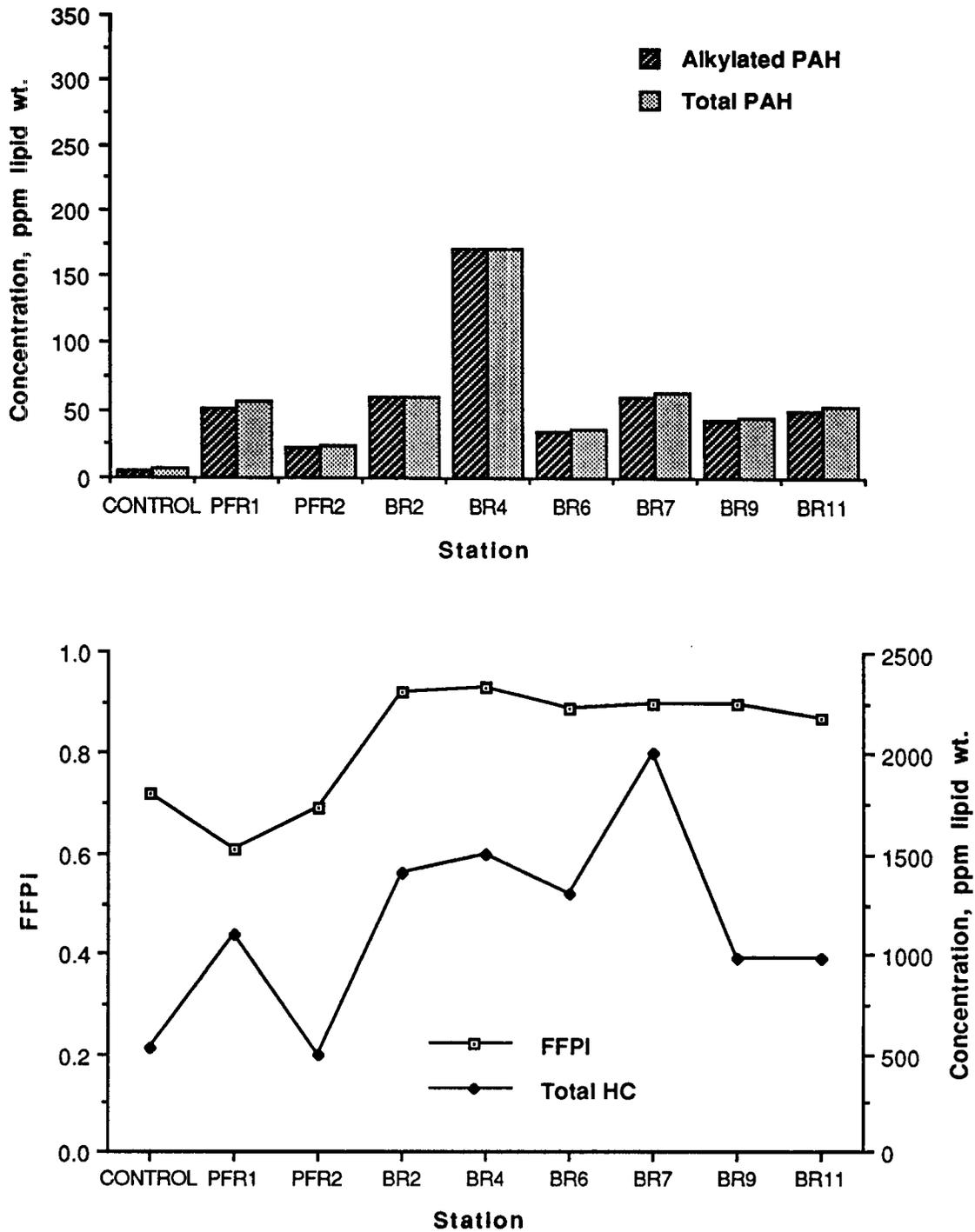


Figure 12.9. Bioaccumulation of PAH and total HC and calculated values of FFPI for oysters deployed in Bayou Rigaud for 27 days in May 1990. Station locations in Figures 12.1 and 12.3.

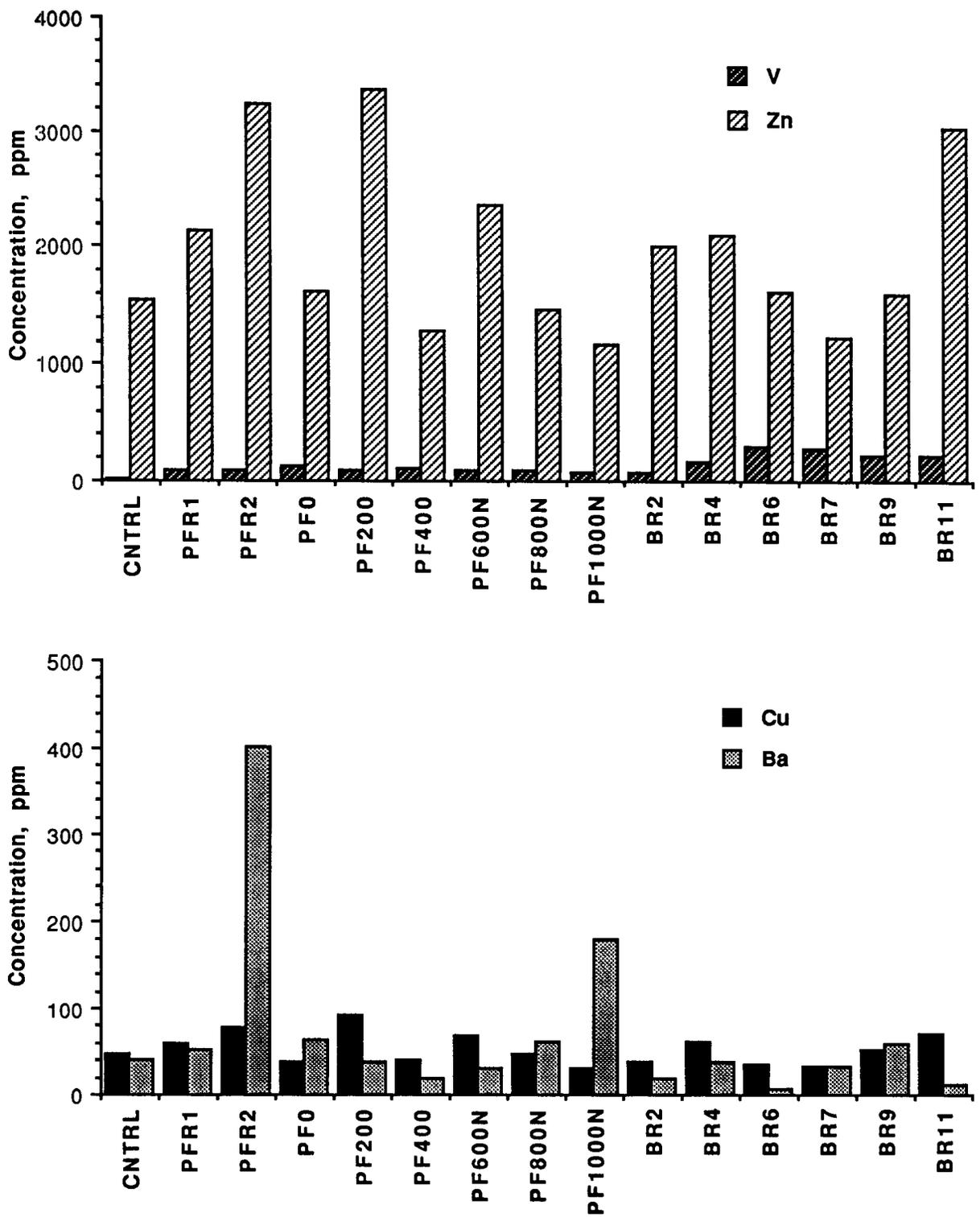


Figure 12.10. Bioaccumulation of selected trace metals for oysters deployed in Pass Fourchon and Bayou Rigaud for 14 days in April 1990. Station locations in Figures 12.1 - 12.3.

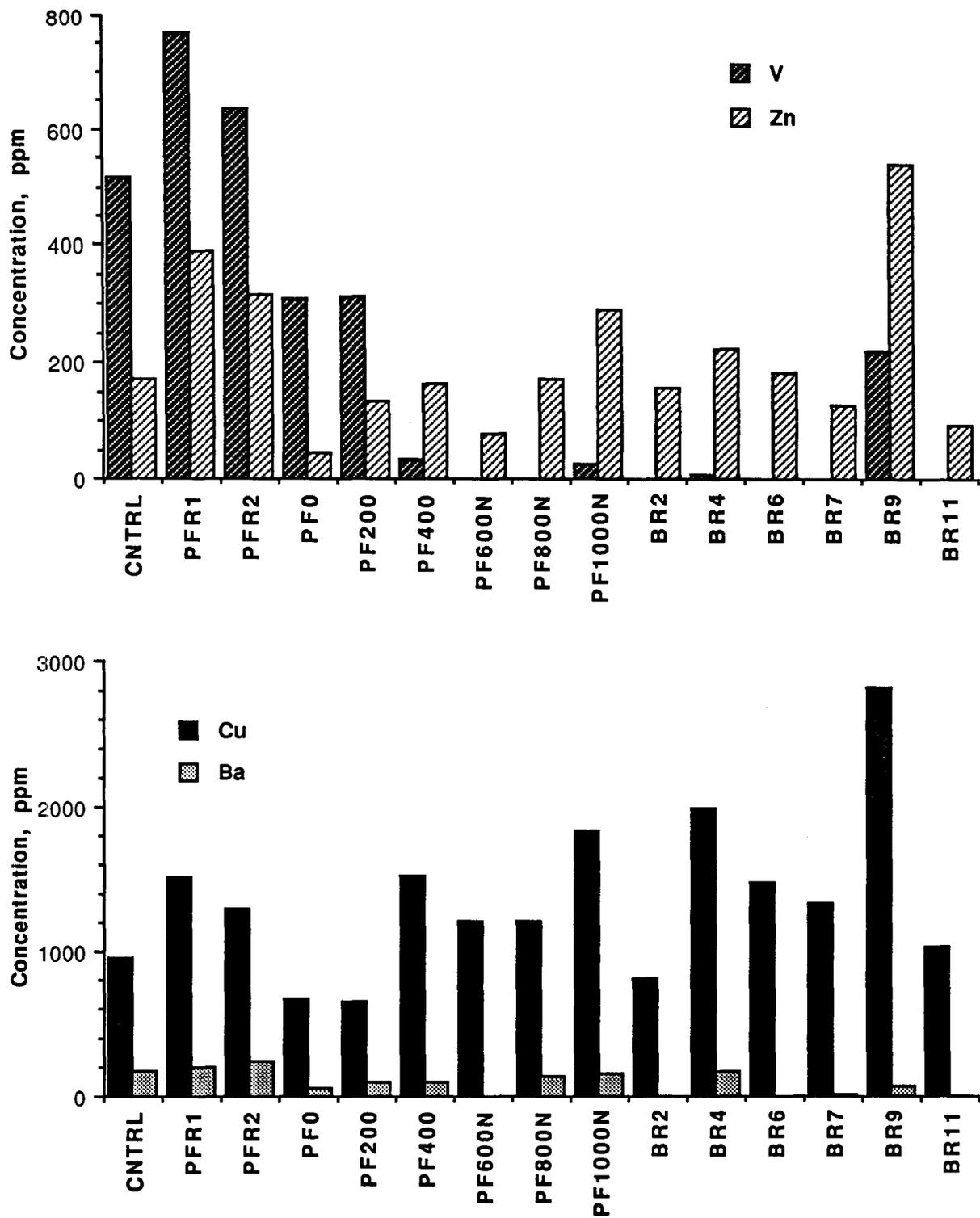


Figure 12.11. Bioaccumulation of selected trace metals for oysters deployed in Pass Fourchon and Bayou Rigaud for 27 days in May 1990. Station locations in Figures 12.1 - 12.3.

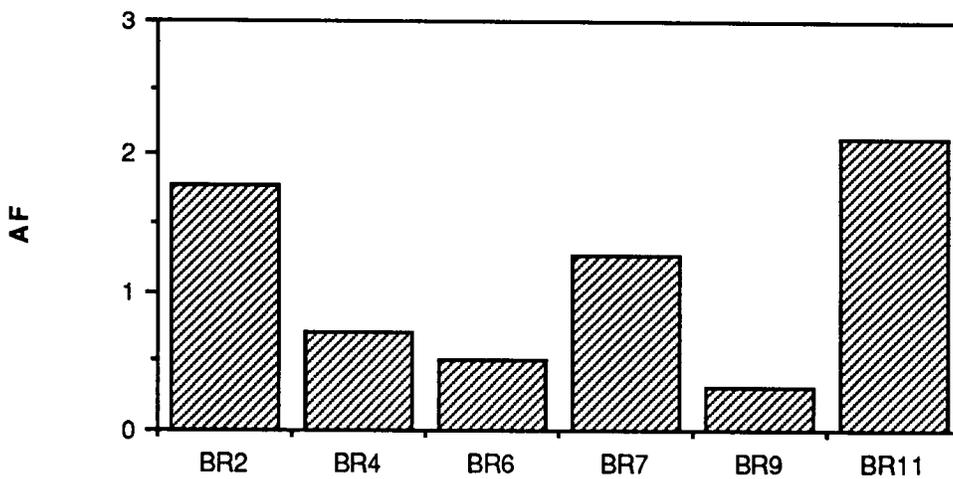
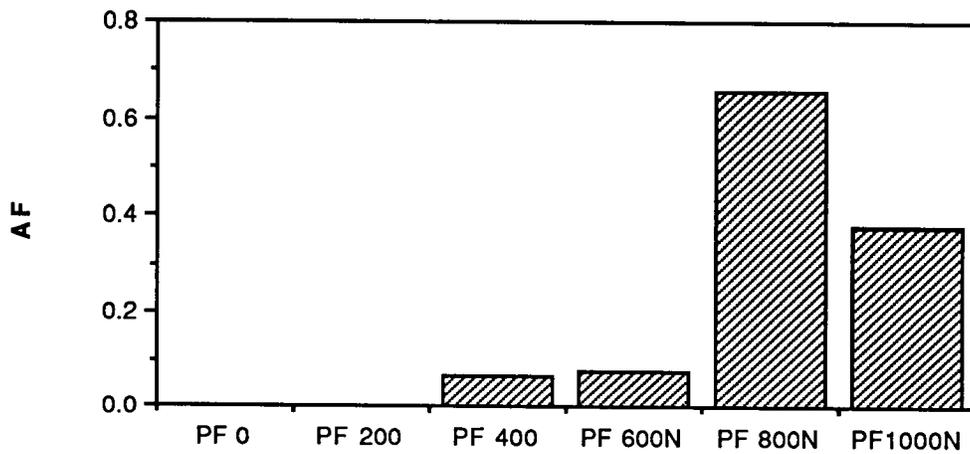


Figure 12.12. Calculated Accumulation Factor (AF) for oysters deployed at Pass Fourchon (PF) and Bayou Rigaud (BR) for Deployment I based on February 1990 sediment data. Station locations in Figures 12.1 - 12.3.

Table 12.1. Conductivity, salinity, temperature and depth information for oyster deployments and recoveries.

Station	Date	Depth (m)	Temperature (°C)	Conductivity (µmhos)	Salinity (ppt)
<u>Deployment I</u>					
PFR1	3/29/90	1.5	26.0	28,500	20.5
PFR2	3/29/90	1.0	24.0	28,000	20.0
PF0	3/29/90	1.3	24.0	29,000	21.0
PF200	3/29/90	1.3	25.0	29,500	21.0
PF400	3/29/90	1.0	24.0	29,000	20.5
PF600N	3/29/90	1.3	25.5	29,000	21.0
PF800N	3/29/90	1.0	25.0	28,500	20.5
PF1000N	3/29/90	1.3	25.0	28,000	20.0
BR2	3/29/90	1.5	22.0	24,500	17.0
BR4	3/29/90	1.5	22.0	23,500	16.5
BR6	3/29/90	1.3	22.0	24,000	17.0
BR7	3/29/90	1.0	22.0	24,500	17.0
BR9	3/29/90	1.0	22.0	24,000	16.5
BR11	3/29/90	1.0	22.0	23,500	16.5
<u>Deployment I Recovery</u>					
PFR1	4/12/90	0.8	20.5	30,500	20.0
PFR2	4/12/90	1.0	22.5	29,500	19.5
PF0	4/12/90	1.0	20.5	28,000	18.5
PF200	4/12/90	1.3	21.0	28,500	19.0
PF400	4/12/90	1.0	22.0	30,000	20.0
PF600N	4/12/90	1.0	21.0	29,000	19.0
PF800N	4/12/90	0.8	23.0	29,000	19.0
PF1000N	4/12/90	1.0	21.0	29,500	19.5
BR2	4/12/90	0.8	20.0	25,000	16.5
BR4	4/12/90	1.0	20.0	25,000	16.5
BR6	4/12/90	0.8	21.0	25,000	16.5
BR7	4/12/90	0.5	20.0	24,500	16.0
BR9	4/12/90	0.5	19.0	23,000	15.0
BR11	4/12/90	0.8	19.5	20,500	13.5
<u>Deployment II</u>					
PFR1	4/27/90	1.0	27.0	26,000	22.0
PFR2	4/27/90	1.0	26.5	26,000	21.5
PF0	4/27/90	1.0	27.0	28,500	21.5
PF200	4/27/90	1.5	28.0	28,000	21.0
PF400	4/27/90	1.0	27.5	29,000	21.5
PF600N	4/27/90	1.0	28.0	27,000	20.0
PF800N	4/27/90	1.0	28.0	27,000	20.0
PF1000N	4/27/90	1.0	27.5	25,000	19.0
BR2	4/27/90	1.0	25.0	22,000	16.5
BR4	4/27/90	1.3	24.5	21,500	16.0
BR6	4/27/90	1.0	25.0	20,500	15.0
BR7	4/27/90	0.8	25.0	20,000	14.5
BR9	4/27/90	1.0	24.5	19,500	14.5
BR11	4/27/90	1.0	24.5	20,000	14.5

Table 12.1.Continued.

Station	Date	Depth (m)	Temperature (°C)	Conductivity (µmhos)	Salinity (ppt)
<u>Deployment II Recovery</u>					
PFR1	5/24/90	1.0	28.0	35,000	21.0
PFR2	5/24/90	1.0	30.0	37,000	22.0
PF0	5/24/90	0.8	28.0	35,500	21.5
PF200	5/24/90	1.0	28.5	35,500	21.5
PF400	5/24/90	1.0	28.0	36,000	21.5
PF600N	5/24/90	1.0	28.5	36,500	22.0
PF800N	5/24/90	0.8	n/a	n/a	n/a
PF1000N	5/24/90	1.0	29.5	36,500	22.0
BR2	5/24/90	1.0	27.5	26,000	15.0
BR4	5/24/90	1.0	28.0	26,000	15.0
BR6	5/24/90	0.8	27.0	26,000	15.0
BR7	5/24/90	0.8	27.0	26,000	15.0
BR9	5/24/90	1.0	27.0	26,000	15.0
BR11	5/24/90	1.0	27.0	26,000	15.0

n/a: not available, meter not working correctly

Table 12.2. Percent mortality in oysters deployed in Pass Fourchon and Bayou Rigaud, Deployment I in April 1990 and Deployment II in May 1990.

Station	# Deployed	# Recovered Alive	# Recovered Dead	% Mortality
Deployment I				
PFR1	26	25	1	3.8
PFR2	26	24	2	7.6
PF0	22	16	6	27
PF200	24	21	3	13
PF400	23	22	1	4.3
PF600N	24	23	1	4.2
PF800N	24	21	3	13
PF1000N	25	22	3	12
BR2	24	22	2	8.3
BR4	22	22	0	0
BR6	23	20	3	13
BR7	24	24	0	0
BR9	22	22	0	0
BR11	24	23	1	4.2
Deployment II				
PFR1	17	16	1	5.8
PFR2	16	13	3	19
PF0	15	8	7	47
PF200	15	11	4	27
PF400	16	11	5	31
PF600N	15	12	3	20
PF800N	15	15	0	0
PF1000N	17	15	2	12
BR2	14	12	2	14
BR4	15	13	2	13
BR6	16	14	2	12
BR7	16	13	3	19
BR9	17	17	0	0
BR11	16	12	4	25

Table 12.3. Percent weight change in oysters deployed in Pass Fourchon and Bayou Rigaud for 14 (Deployment I) and 27 (Deployment II) days.

Site	% Wt. Chg.	Site	% Wt. Chg.	Site	% Wt. Chg.	Site	% Wt. Chg.
Deployment I				Deployment II			
PFR1	1.5%	PFR2	3.5%	PFR1	17.1%	PFR2	Dead
PFR1	8.5%	PFR2	6.9%	PFR1	Dead	PFR2	9.6%
PFR1	4.1%	PFR2	15%	PFR1	15.6%	PFR2	7.8%
PFR1	10.0%	PFR2	7.1%	PFR1	11.7%	PFR2	21%
PFR1	4.8%	PFR2	4.8%	PFR1	7.3%	PFR2	6.7%
PFR1	1.1%	Mean±SD	7.4%±4.3%	Mean±SD	13%±4.4%	Mean±SD	11%±6.7%
Mean±SD	5.0%±3.6%						
PF0	0.0%	BR2	3.9%	PF0	Dead	BR2	Dead
PF0	-1.6%	BR2	3.7%	PF0	Dead	BR2	10%
PF0	1.7%	BR2	9.0%	PF0	2.2%	BR2	6.3%
PF0	Dead	BR2	9.1%	PF0	2.4%	BR2	Dead
PF0	1.5%	BR2	7.7%	PF0	Dead	BR2	10%
Mean±SD	0.4%±1.5%	BR2	6.5%	Mean±SD	2.3%±0.2%	Mean±SD	8.8%±2.3%
		Mean±SD	6.7%±2.4%				
PF200	6.7%	BR4	6.4%	PF200	Dead	BR4	12%
PF200	1.9%	BR4	13%	PF200	Dead	BR4	Dead
PF200	2.7%	BR4	6.3%	PF200	6.2%	BR4	15%
PF200	2.3%	BR4	3.8%	PF200	0.9%	BR4	13%
PF200	3.4%	BR4	3.6%	PF200	1.5%	BR4	6.6%
PF200	0.7%	Mean±SD	6.6%±3.7%	Mean±SD	2.9%±2.9%	Mean±SD	11%±3.5%
Mean±SD	3.0%±2.0%						
PF400	3.0%	BR6	5.7%	PF400	8.1%	BR6	6.9%
PF400	5.8%	BR6	8.3%	PF400	20%	BR6	4.2%
PF400	1.3%	BR6	5.9%	PF400	7.4%	BR6	10%
PF400	-2.3%	BR6	2.4%	PF400	7.8%	BR6	15%
PF400	4.2%	BR6	5.0%	PF400	2.2%	BR6	7.3%
Mean±SD	2.4%±3.1%	Mean±SD	5.5%±2.1%	Mean±SD	9.1%±6.6%	Mean±SD	8.9%±4.3%
PF600N	5.2%	BR7	7.7%	PF600N	8.0%	BR7	16%
PF600N	4.2%	BR7	6.6%	PF600N	8.8%	BR7	14%
PF600N	4.5%	BR7	7.3%	PF600N	Dead	BR7	13%
PF600N	8.6%	BR7	4.2%	PF600N	12%	BR7	37%
PF600N	1.8%	BR7	4.2%	PF600N	Dead	BR7	15%
PF600N	1.4%	BR7	5.6%	Mean±SD	9.4%±1.9%	Mean±SD	19%±10%
Mean±SD	4.3%±2.6%	Mean±SD	5.9%±1.5%				
PF800N	2.5%	BR9	1.8%	PF800N	22%	BR9	7.1%
PF800N	10%	BR9	3.3%	PF800N	5.4%	BR9	9.1%
PF800N	9.2%	BR9	7.3%	PF800N	19%	BR9	10%
PF800N	2.0%	BR9	3.5%	PF800N	17%	BR9	15%
PF800N	7.4%	BR9	7.7%	PF800N	14%	BR9	15%
Mean±SD	6.3%±3.8%	Mean±SD	4.7%±2.6%	Mean±SD	15%±6.3%	Mean±SD	11%±3.6%
PF1000N	5.8%	BR11	4.7%	PF1000N	16%	BR11	Dead
PF1000N	8.0%	BR11	2.5%	PF1000N	6.6%	BR11	13%
PF1000N	0.7%	BR11	0.0%	PF1000N	9.7%	BR11	12%
PF1000N	6.8%	BR11	3.5%	PF1000N	9.2%	BR11	8.3%
PF1000N	4.5%	BR11	2.6%	PF1000N	Dead	BR11	13%
Mean±SD	5.2%±2.8%	BR11	3.4%	Mean±SD	10%±4.0%	Mean±SD	12%±2.3%
		Mean±SD	2.8%±1.6%				

Chapter 13

SYNTHESIS

13.1 Introduction

The results from this study represent the most comprehensive and detailed analyses to date of the fate and effects of produced waters in coastal environments. Of the 15 facilities which discharge OCS-generated produced water into coastal environments of Louisiana, 10 discharges in seven areas were studied (Tables 2.1 and 2.2, Figure 2.1). The volumes of the discharges in the study areas are larger than most for coastal Texas and Louisiana, and a variety of receiving environments was represented. The volumes of discharges examined in this study ranged from 3,000 to 106,000 bbl·d⁻¹. [The modal class for produced water discharges into Louisiana waters is 100 to 500 bbl·d⁻¹, and only 10% of the reported discharges are greater than 5,000 bbl·d⁻¹ (Boesch and Rabalais 1989a).] The total discharges of both OCS- and State-generated produced waters for the study areas are also large and range from 3,700 bbl·d⁻¹ to 146,000 bbl·d⁻¹ (Table 13.1). While few in number, facilities that discharge OCS produced waters into coastal environments of Louisiana account for large volumes, individually and collectively, and represent 13% of all produced waters discharged into the State's waters.

The receiving environments for these effluents are varied and include: the shallow, nearshore continental shelf; high energy, freshwater distributaries of the Mississippi River delta; and brackish to saline coastal environments with moderately to poorly flushed waters. All study areas are within the Mississippi River Deltaic Plain. Small volume discharges on the southwestern Louisiana coast, as well as a large volume discharge in Southwest Pass of the Mississippi River were excluded from the study (see Chapter 2). This study expanded on the initial assessment of Boesch and Rabalais (1989a) with increased temporal and spatial studies of three areas, additional study areas including an abandoned discharge, and additional analytical and field observations.

In each area, an assessment of the fate and effects of produced water discharges was made along with a detailed analysis of the effluent. The receiving environment was characterized with respect to hydrographic regime and the sedimentary characteristics. Hydrographic profiles, interstitial salinity of surface sediments and near-bottom water contaminants were examined to determine the extent of the brine effluent and its chemical constituents. Likewise, surficial sediments were examined to assess the extent and composition of chemical contamination. Vertical sediment cores provided information on the long-term accumulation of chemicals. Biological assessments included benthic community analyses and the bioaccumulation of produced water origin contaminants.

The results from each study area have been summarized in the respective chapters. In this chapter, we provide an overall synthesis of the results from the study. Several factors determine the fate and effects of produced waters in coastal environments and organisms. These include the volume and composition of the discharge and the hydrologic, biological and physical characteristics of the receiving environment. Comparisons among the study areas are made in subsequent sections and are summarized in Tables 13.1 - 13.4. We also re-examine the questions posed in Chapter 1 concerning the dispersal of contaminants and the effects of these contaminants in the environment.

13.2 Comparison of Effluents

While the focus of this study was the discharge of OCS-generated produced waters in coastal Louisiana, the treatment facilities were very often located in close proximity to other OCS-source effluents and/or effluents from product streams generated in State waters. Table

13.1 compares the total discharges for each of the study areas, both OCS-generated and State-generated. These total daily discharges indicate that large volumes enter any single receiving environment in the range of 3,700 to 146,000 bbl·d⁻¹ from one or as many as four facilities. The arrangement of study areas in Table 13.1 is in order of decreasing total daily discharges. This order is duplicated in subsequent tables for comparative purposes.

Results in Chapter 4 provide the most detailed analyses to date for produced water effluents. Produced water discharges vary greatly in the amounts of organic and inorganic compounds. Similar compounds are found in each of the effluents, but the relative proportions differ with the facility and through time. Differences among facilities are related to the product streams which may come from multiple formations and to differences in treatment technologies. Temporal changes in concentrations of the various chemical constituents are related to changing chemistry of the product that is being treated, varying proportions of multiple and chemically different sources, changes in treatment technology, and efficiency of the separation. Comparison of the Exxon discharge "Pre" and "Post" aeration pond samples indicated a reduction in the concentrations of volatile hydrocarbons, acid-extractable compounds and polynuclear aromatic hydrocarbons and Pb-210 activity, but not trace metals and total radium activity. These differences were attributed to aeration of volatiles and additional settling of particle-adsorbed contaminants in an open maze pond after gravity separation. For the remaining facilities, we do not have adequate information on treatment technologies to assess their effects on temporal differences within a discharge and among discharge points. Trace metal concentrations and total radium activity were fairly consistent through time for the discharges. Pb-210 activity, on the other hand, showed variability. Total radium activities were positively related to the salinity of the effluents; salinity was consistent for a discharge. Pb-210 is very particle-reactive and the temporal changes in the Pb-210 activities of the water samples may be related to the settling out of particulate material during the treatment process.

Comparisons of the produced water discharges can be approached additionally by calculations of loadings of particular contaminants. Examples of PAH daily discharge rates for the individual effluents and totals for study areas were provided in Chapter 4 (Figure 4.24). Similarly, the loadings of these and other constituents can be combined for all discharge points in a single study area (Table 13.1). High concentrations of a single component, e.g., VH or Ba, may be compensated for by a lower volume discharge; or vice versa, a contaminant may not be particularly concentrated in the effluent, but the volume may be large and the total loading may be similarly large. These comparisons provide a context for the relative contribution of contaminants to a receiving environment which may be traceable in the environment. For example, loadings of VH were large for Bayou Rigaud (primarily the result of the large volume) and Eugene Island Block 18 (primarily the result of high concentrations in the effluent) (Table 13.1). Detectable levels of VH were found in overlying waters at both of these study areas. In spite of a high dilution potential at Eugene Island Block 18 (Table 13.2), there were detectable levels of several VH at some distance from the discharge; the net loading of these constituents was important in their retention in the water column. Mass loadings of VH were also high in the Pass Fourchon study area; this combined with a poorly flushed water column contributed to the retention of these contaminants in a density plume for some distance from the discharge. Loadings of VH were much lower for the remaining study areas. Of the five remaining areas, elevated levels of VH were found only at a single station at East Timbalier Island in a dead-end canal near the discharge point. The lack of flushing in this particular point compared to the moderately- to well-flushed characteristics of the other areas would account for VH contamination even though loadings were relatively low.

Similar comparisons can be made for the other chemical constituents in Table 13.1. These produced water contaminants, however, are particle reactive and their eventual dispersion depends on the sedimentary regime of the receiving environment and the likelihood of sediment resuspension and transport. Bayou Rigaud ranks highest in the mass loadings of total PAH, Ba

and Pb-210. Ranking of areas by Pb-210 loadings follows the decreasing order of total daily discharge volumes. For PAH and Ba, the ranking of areas by loadings is related to a combination of volume of the discharge and concentration of the constituents.

13.3 Comparison of Receiving Environments

An evaluation of the hydrological and sedimentological characteristics of each study area was made to determine the dilution potential of the environment for the produced water effluents (Table 13.2). Dilution of water soluble contaminants would be influenced primarily by the volume of the receiving waters and the current velocity. With the exception of measurements taken on a high spring tide (Empire Waterway) and during a storm (Romere Pass and Eugene Island Block 18 in May 1989), current velocity measurements taken on discrete 25-hr periods were assumed to be representative of similar conditions throughout the year.

Dispersion of sediment-adsorbed contaminants would be influenced by the bed shear stress, proportional to the slope of the current velocity profile (potential for resuspension and transport), sedimentation rates, and the grain size distribution of the surface sediments. Because influx of Pb-210 greatly exceeded the natural decay rate for all the study areas, sedimentation rates could not be calculated. Accumulation of sediments was concluded from grain size distributions and/or surface sediment and downcore chemical contamination.

Two environments are characterized as having a high potential for dilution of contaminants: Emeline Pass and Eugene Island Block 18. Mean current velocities reach $9 \text{ m}\cdot\text{s}^{-1}$ in Emeline Pass, and the coarse-grained, low organic content sediments indicate active sediment transport close to the bed. Eugene Island Block 18 is located in open, shallow offshore waters adjacent to the Atchafalaya River delta. High freshwater flow influences the area, and the shallow, inner continental shelf is expected to be subject to wind-induced events causing resuspension and rapid turnover of surficial sediments. On the other end of the continuum is the Pass Fourchon study area. Current velocities are consistently negligible; potential for sediment entrainment and transport is low. The sediments within the dead-end canal system are sandy muds or muddy sands. Abrupt transitions within the study site are apparent in increasing sand content at the station in closest proximity to the back of the sandy barrier shoreline and at those stations in the more tidally active Belle Pass.

The remainder of the environments were characterized as having a medium potential for dilution of produced water contaminants. Current velocities were strong in Bayou Rigaud and sufficient to resuspend and transport sediments during peak tidal flow. The sedimentary regime, however, indicated periods of high silt content. Alterations in sediment grain size composition would indicate periods of accumulation and periodic resuspension related to storms. A similar situation was found in Empire Waterway. Tidal currents were strong when measured (as noted above on a high spring tide) and indicated that potential for sediment resuspension and transport was high. However, the high silt content of the sediments and the accumulation of contaminants near the abandoned discharge point indicated a depositional environment. Resuspension of sediments and shifts in sediment grain size distribution would be storm related as in Bayou Rigaud. In Romere Pass, sediments were sands, but fine-grained, and graded to silts on the northern end of the transect. Resuspension events in Romere Pass would be seasonal and related to the flow of the Mississippi River rather than storm related as in Bayou Rigaud and Empire Waterway. Two hydrological and sedimentary environments can be distinguished at the East Timbalier Island study site. Current velocities, during the single sample period, indicated moderate flushing in the east-west canal where siltier sediments occurred. The north-south access canal was less well flushed, had sandier sediments similar to a back barrier regime, and contained higher levels of sediment-adsorbed contaminants.

13.4 Dispersion of Brine Effluent

Because produced water effluents have salinity levels in excess of that of ambient sea water and may act as a dense plume upon discharge into receiving waters, the salt content of the bottom waters may sometimes be used as a conservative tracer of the brine plume. A clear density plume was identifiable only at the Pass Fourchon study area, and extended up to 800 m from the point of discharge (Table 13.2). Elevated salinity was found in the bottom water at a single station in the East Timbalier Island study area and was related to the produced water effluent. Otherwise, no clear salinity signals were found that could be attributed to a produced water effluent. Elevated interstitial water salinities of surface sediments identified the same stations at Pass Fourchon and East Timbalier Island as being affected by the salinity plume.

Other tracers of the produced water effluent (VH, total Ra and sulfide) are water soluble and are not conservative, but their presence in near-bottom waters would indicate the extent of the produced water plume to at least the distance they were detected. In the case of VH, the extent of contamination of the overlying water column by these chemicals was the same as the salinity signal for Pass Fourchon and East Timbalier Island. At Eugene Island Block 18, elevated VH in near-bottom waters were detected adjacent to the discharge and to some distance from the discharge whereas an elevated bottom water salinity was not. Sulfide levels were elevated in some of the near-bottom waters at Pass Fourchon; one of the effluents for the study area was high in sulfide. Elevated levels of sulfides in the near-bottom waters of some stations in the Romere Pass study site may be related to an effluent with a high sulfide content. Sulfides were not elevated in the remaining produced water discharges; but where an effluent contained high sulfides, there were indications that this constituent may be traced in the environment.

The levels of total radium activity in the near-bottom waters potentially provide information concerning the dispersion of water column contaminants in addition to the salinity, VH, or sulfide tracers. At the Pass Fourchon study area, total radium activity was elevated above background level to a distance of 1000 m from the discharge point. VH and salinity signals were detectable only within 800 m of the discharge point. Elevated radium levels were detected at Bayou Rigaud, but there was no clear pattern to the distributions. At Eugene Island Block 18, higher total Ra activities paralleled the elevated levels of VH. In Romere Pass, total Ra three times above natural levels was detected at RP1000N (450 m from the discharge point) where there were no detectable levels of VH or elevated salinity. For both the East Timbalier Island and Empire Waterway study sites, total Ra activities were elevated well above background levels throughout the study areas. This indicates some level of water column contamination which was not indicated by the other tracers.

13.5 Sediment Contamination

13.5.1 Surface Sediments

A comparison was made by study area of the ratio of contaminants to background levels and the distance from the discharge point where a sediment contaminant signal was identifiable (Table 13.3). The ratios were calculated by comparing the maximum sediment contamination to the background (or lowest) level in the study area. Where there was more than one sample period, both the maximum concentrations and background levels were averaged. Distance of contaminant effect was determined as the greatest distance where the concentration of the constituent was elevated above background levels or the FFPI (fossil fuel pollution index) indicated petrogenic origin hydrocarbons.

High ratios could be influenced by several factors. First, the concentration of the constituents may be high in the effluent. For example, the effluent at Eugene Island Block 18 was high in Ba and the ratio of concentrations in the sediments to background levels is similarly

high. Second, the background level calculations may include stations with sandy sediments where concentrations would be lower; several of the study areas had dramatic differences in sediment grain size characteristics between stations. For example, the high concentration ratio of Ba at the Pass Fourchon area would be attributed to low background levels in sandy sediments at the distal ends of the study transect. Ratios may be low for different reasons. In Bayou Rigaud where there are large loadings of Ba (Table 13.1), the concentration ratio is low because Ba was found in elevated levels throughout the study area. Still, the concentration ratios (Table 13.3) provide an index for comparison among study areas of the heavily contaminated sediments and provides a context for the contamination of the sediments within the receiving environment of the individual areas.

The extent to which sediment contamination was documented in distance from a discharge point is a function of the loadings of the contaminant (Table 13.1), the nature of the receiving environment (Table 13.2), and the partitioning of the chemical constituent in the environment. With the exception of the Bayou Rigaud study area, Ba was detected at least as far as or to greater distances from the discharge point than alkylated PAH and Pb-210 (Table 13.3). Because of inconsistent gradients of Ba with distance from the discharge, characteristics of the geochemistry of Ba, or additional inputs to the systems from drilling fluids, Ba is not a particularly good tracer of sediment-borne hydrocarbon contaminants. With the exception of the Bayou Rigaud and Empire Waterway study sites, Pb-210 was found at elevated levels at equal to or less distances from the discharge point than elevated levels of PAH. Pb-210 is, therefore, not a particularly good tracer of sediment-borne hydrocarbon contaminants either. The concentration ratios of maximal Pb-210 concentrations to background levels were less than 10:1 compared to ratios of usually > 100:1 for alkylated PAH (Table 13.3). The fate of produced water source hydrocarbons are, therefore, best determined from direct measurements of these constituents.

With the exception of the Emeline Pass study area and the active discharge facility at Empire Waterway, elevated levels of alkylated PAH were found in the sediments at all the study areas (Table 13.3). The location of the discharge in both of these study areas may account for lack of a contaminant signal in the receiving environment. Emeline Pass also has the added feature of being a high energy, river-dominated environment which would rapidly dilute any effluent which may enter the system. Elevated levels of alkylated PAH were found to the maximal distances of the study transects at both Bayou Rigaud and Pass Fourchon, 1300 and 1000 m, respectively. More limited distances of elevated levels were found for alkylated PAH at Romere Pass (450 m), East Timbalier Island (250 m), Eugene Island Block 18 (250 m) and the abandoned discharge at Empire Waterway (250 m).

13.5.2 Vertical Sediment Profiles

The concentration of hydrocarbons, trace metals and Pb-210 were analyzed for several vertical sediment cores at several of the study areas and for different time periods at some of them. Pb-210 activities in the vertical sediment profiles were not appropriate for calculation of sedimentation rates. Some decay in Pb-210 must be present with depth to calculate a sedimentation rate. The profiles obtained indicated either an increase in activity levels with depth or inconsistent variability with depth. We concluded that the profiles were influenced by several factors including varying input and disturbance of the sedimentary structure by dredging, boat traffic, and/or natural events. This explanation is consistent with the hydrocarbon contamination seen in some of the vertical cores which indicates maxima in produced water origin hydrocarbons both subsurface and/or with depth in the core. Such non-uniform distributions indicate varying inputs of contaminants to the bed sediments.

Hydrocarbon concentrations in vertical cores indicated 1) a decrease in overall concentrations with increasing distance from the produced water discharge point, 2) maximal

concentrations in the upper sections of the cores at those stations closest to the discharge point, 3) subsurface maxima and additional maxima with depth in cores separated by lower concentrations in intervening sections, particularly in those closer to the discharge points, 4) very often a weathering of saturated hydrocarbons with depth in the core, and 5) elevated levels of hydrocarbons in the upper sections of vertical cores collected from the distal ends of study area transects usually indicative of pyrogenic hydrocarbon inputs. Changes in concentration of produced water hydrocarbons with depth in vertical cores are related to changes in mass loadings through time, variations in transport and deposition of contaminated sediments, resuspension and transport of contaminated sediments from the area during storm events, and transport of uncontaminated sediments into the area during storm events. The presence of high concentrations of produced water derived hydrocarbons to depths of 25 to 30 cm in a vertical sediment core in some of the study areas indicates the long-term accumulation of these contaminants and their resistance to degradation.

13.5.3 Abandoned Discharge

The study site at Empire Waterway included an abandoned discharge. The Pelican Island facility discontinued a discharge of approximately 12,000 to 15,000 bbl·d⁻¹ in 1987. When the photomission was flown in November 1988, the facility was being dismantled; when sampled in November 1989, the marsh was being restored. Based on aerial photographs and communications with industry representatives, the point of the produced water discharge was determined to be near a pit along a slough in the marsh, somewhat removed from the dredged access canal. The closest station sampled was 250 m from the discharge point.

Alkylated PAH were detected at low concentrations at several stations along the transect adjacent to the abandoned discharge facility. In contrast, no significant levels of alkylated PAH were detected in any of the sediments along the transect near the active discharge. The maximum value was found at a station approximately 250 m from the discharge point at the Pelican Island facility, and concentrations decreased away from this point.

Vertical sediment cores analyzed from this site showed maximal petrogenic contamination in surface sections, either 0-2 cm or 2-5 cm. In fact, the 2-5 cm section of the core from the station closest to the abandoned discharge point had the highest concentration of alkylated PAH for the entire Empire Waterway study area. Subsurface elevated levels of alkylated PAH of petrogenic origin were found in 20-25 cm sections of cores closest to the discharge point and to some distance from the discharge point. Despite the categorization of this study area as medium for dilution potential, the sediments accumulate but are periodically resuspended and transported from the area (or into the area). The presence of produced water hydrocarbons in relatively high concentrations with depth in the vertical cores indicates the long-term accumulation of these constituents and their resistance to degradation in the sediments.

13.6 Biological Effects and Bioaccumulation

Biological assessments of the impact of the produced water effluents were determined as changes in benthic communities along a gradient of distance from the discharge point(s) within each study area and by bioaccumulation studies of filter-feeding bivalves in a similar gradient at Pass Fourchon and Bayou Rigaud. The generalized results from these studies are shown in Table 13.4. Analysis of variance indicated statistically significant differences among the station means of the number of species per replicate and number of individuals per replicate for most study sites. Duncan's multiple range tests of the station means within each study area indicated that some groups of stations were distinct from others with regards to impacted fauna, but more often there was a gradient in impacts with distance from the discharge indicated by overlapping station means. Those station means that were distinctly different from other stations are labeled "Distinct" in Table 13.4; those with an overlap in the station means are labeled "Gradient." In

three cases, the means for the benthic community parameters differed among stations, but these differences were not related to a distance gradient from the discharge point. These are labeled "No Effect" for both the Distinct and Gradient categories. Effects on benthic communities were generally negative in that they indicated loss of numbers of species and number of individuals when compared to controls. It was not possible to determine from these studies ecological effects such as the manner in which loss of biomass or specific organisms might adversely impact the structure of the ecosystem.

The most severely depressed benthic macroinfaunal communities were found within 500 to 800 m of the discharge point in Pass Fourchon. Because of the position of the ship during benthic collections, the stations at 600 and 800 m from the discharge in Pass Fourchon varied in their representation of impacted communities. Impacts to the benthic communities were observed as far as 700 m in Bayou Rigaud, 300 m at Eugene Island Block 18, 100 m at East Timbalier Island, and within 550 m of the abandoned discharge at Empire Waterway. The impacts of accumulated and residual produced water contaminants adjacent to the abandoned discharge site indicate the persistent effects of these constituents on the benthic fauna. It was not possible to estimate the time required for the affected benthic community to recover from the impact of the produced water, but evidently it exceeded the three years since the cessation of the discharge. No effects on the benthic communities were observed in the Emeline Pass and Romere Pass study areas. Both of these environments, however, were normally low in numbers of species and individuals. Impacts on the benthic macroinfauna were consistent across season in the Pass Fourchon and Eugene Island Block 18 study areas.

Benthic community impacts were associated with distance from the discharge and levels of produced water chemical constituents in the sediments. The threshold concentrations of contaminants at or above which the benthic community was affected varied among study sites (detailed in the appropriate chapters). For example, the threshold level of alkylated PAH for East Timbalier Island was 5,000 ppb; Pass Fourchon, 5,900 ppb; Bayou Rigaud, 7,700 ppb; and Eugene Island Block 18, 430 ppb. These differences are a function of the sedimentary characteristics of the environment and the type of benthic community associated naturally with the environment.

A comparison of accumulation of produced water contaminants in oysters from Pass Fourchon and Bayou Rigaud is shown in Table 13.4. The comparisons are based on Deployment I in April (as opposed to Deployment II in May) as indicative of a predicted moderate level of accumulation compared to expected higher values in winter and the lower values found a month later when the oysters were presumed to be spawning and mobilizing lipids and associated hydrocarbons. Results from the bioaccumulation studies indicated 1) lower weight gain for those oysters deployed close to the discharge point at Pass Fourchon, 2) increased mortality for oysters during the longer deployment and at stations closer to the discharges at Pass Fourchon, 3) accumulation of alkylated PAH and total hydrocarbons in all oysters above background levels in the first deployment, 4) rapid accumulation of contaminants in produced water, 5) variability in accumulation with season and reproductive condition, 6) a decrease in the accumulation of alkylated PAH and total hydrocarbons in May compared to April, 7) levels of accumulated contaminants above the concentrations of contaminants in ambient sediments, 8) inconsistent results for trace metal accumulations, and 9) limited accumulation of radionuclides. The bioaccumulation studies show the clear potential for uptake and accumulation of contaminants in produced water by oysters, both in close proximity to the discharge point and to great distances from the discharge.

Table 13.1. Comparison of produced water discharges by study area. Study areas arranged in order of decreasing total daily discharges of both OCS- and State-generated produced waters.

Study Area	Daily Discharge ^a (bbl·d ⁻¹)	Number of Current Discharges	Mass Loadings ^b			
			VH (kg·d ⁻¹)	PAH (kg·d ⁻¹)	Ba (kg·d ⁻¹)	Pb-210 (dpm·d ⁻¹)
Bayou Rigaud	145,760	2	98.8	10.5	1,030.1	1.02
Pass Fourchon	48,169	3	11.2	3.5	207.2	0.07
East Timbalier Island	25,558	4	1.2	3.6	934.6	0.03
Eugene Island Block 18	21,000	1	19.4	1.4	634.4	0.01
Romere Pass	20,158	2	5.1	3.4	25.7	0.01
Empire Waterway (Current discharge)	10,959	1	2.6	0.9	4.1	<0.01
Emeline Pass	3,693	1	0.5	1.4	14.4	<0.01

^aTotal for study area (from discharges listed in Tables 2.1 and 2.2 for period 02/89 - 02/90).

^bCalculated from average concentrations in effluents, average daily discharges, and conversion of 1 barrel = 159 liters.

Table 13.2. Comparison of study areas with respect to dilution potential of the receiving environment. Study areas arranged in order of decreasing total daily discharges (listed in Table 13.1).

Study Area	Dilution Potential of Environment ^a			Dilution of Plume and Extent ^b
	High	Medium	Low	
Bayou Rigaud	Depositional environment Periodic resuspension (storm related)			No plume observed Limited in previous study
Pass Fourchon	Depositional environment			3 to 6:1 initially 800 m on bottom
East Timbalier Island	Depositional environment/ Erosional environment			3:1 initially 100 m on bottom
Eugene Island Block 18	Depositional environment Periodic resuspension (wind related)			No plume observed
Romere Pass	Depositional environment Seasonal resuspension (river flow related)			No plume observed
Empire Waterway	Depositional environment Periodic resuspension (storm related)			No plume observed
Emeline Pass	Erosional			No plume observed

^aBased on current velocity profiles and sedimentary characteristics.

^bBased on bottom water salinity.

Table 13.3. Comparison of study areas with respect to levels of sediment contamination and distance of elevated contaminants from discharge points. Study areas arranged in order of decreasing total daily discharges (listed in Table 13.1).

Study Area	Concentration Ratio (average maximal level to average background)			Extent of Sediment Contamination (in m from discharge)		
	Ba	Alkylated PAH	Pb-210	Ba	Alkylated PAH	Pb-210
Bayou Rigaud	4:1	130:1	2:1	1,000	1,300	1,000
Pass Fourchon	33:1	390:1	8:1	1,000	1,000	1,000
East Timbalier Island	16:1	1,900:1	4:1	580	360	<100
Eugene Island Block 18	26:1	240:1	2:1	250	250	<50
Romere Pass	6:1	800:1	2:1	450	450	<250
Empire Waterway (Current discharge)	4:1	tr	2:1	1,000	NA	<300
(Abandoned discharge)	2:1	30:1	2:1	1,000	250	<450
Emeline Pass	8:1	20:1	4:1	<100	<100	<100

NA - not applicable.
tr - trace.

Table 13.4. Comparison of study areas with respect to biological effects; extent of effect given in meters from discharge point. Study areas arranged in order of decreasing total daily discharges (listed in Table 13.1).

Study Area	Type of Effect	Benthic Community Differences				Bioaccumulation*	
		Species Effect	Extent (m)	Individuals Effect	Extent (m)	Amount	Extent (m)
Bayou Rigaud	Distinct Gradient	Yes	150	No	---	High	200
		Yes	500	Yes	700	Moderate	1,000
Pass Fourchon	Distinct Gradient	Yes	500	Yes	500	High	350
		Yes	800	Yes	800	Moderate	300
East Timbalier Island	Distinct Gradient	Yes	100	Yes	100		
		No	---	No	---		
Eugene Island	Distinct Gradient	No	---	Yes	<50		
		Yes	300	Yes	300		
Romere Pass	Distinct Gradient	No	---	No	---		
		No	---	No	---		
Empire Waterway (Current)	Distinct Gradient	No	---	No	---		
		No	---	No	---		
(Abandoned)	Distinct Gradient	No	---	No	---		
		Yes	250	Yes	<550		
Emeline Pass	Distinct Gradient	No	---	No	---		
		No	---	No	---		

*Based on Deployment I.

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